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The lattice spacings of solid solutions of different elements in aluminium

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(Received 14 August 1947—Read 12 February 1948)

Measurements have been made of the lattice spacings of solid solutions of lithium, magnesium, silicon, copper, zinc, germanium and silver in aluminium. The lattice of aluminium is expanded by the solution of magnesium or germanium, and contracted by the solution of lithium, silicon, copper or zinc. No change in lattice spacing can be detected when silver is dissolved in aluminium, although microscopic examination shows that a solid solution is formed, and this is confirmed by the absence of any diffraction lines other than those of the solid solution in aluminium.

If the lattice spacing/composition curve for dilute solutions is extrapolated to 100% of solute, the resulting lattice spacing refers to a hypothetical face-centred cubic modification of the solute, and the corresponding closest distance of approach of the atoms is called the apparent atomic diameter (A.A.D.) of the solute when in solution in aluminium. Previous work enables the corresponding A.A.D. values to be deduced for the above solute elements when dissolved in univalent copper, silver or gold, and in divalent magnesium. The differences between the A.A.D. values of a given element when dissolved in various solvents are discussed, and it is suggested that they are controlled by the interplay of four factors: (1) the relative volume per valency electron in crystals of the solvent and solute, (2) the relative radii of the ions of solvent and solute, (3) Brillouin zone effects, and (4) the difference between solvent and solute in the electrochemical series. If this line of approach adopted be correct, it follows that it is only in exceptional circumstances that the so-called Vegard's law will apply to metallic solid solutions.

1. INTRODUCTION

The lattice spacings of solid solutions of different elements in copper and silver were investigated by Hume-Rothery, Lewin & Reynolds (1936), and later by Owen & Roberts (1939), who also examined solid solutions in gold (1945). In these alloys the solvent metal is univalent and the electron states of the first Brillouin zone are only half filled. The experimental results show that for any one solvent the lattice distortion produced by a given atomic percentage of the solutes in any one row of the periodic table (e.g. Ag, Cd, In, Sn, Sb) increases algebraically with the valency of the solute. The lattice spacings of solid solutions in magnesium were investigated by Hume-Rothery & Raynor (1940*a*), and by Raynor (1942). In these alloys the solvent metal is divalent, and with two valency electrons per atom, overlapping has occurred in some directions of the first Brillouin zone of the close-packed hexagonal structure. In the magnesium-rich alloys, the addition of relatively small amounts of solute of higher valency produces an overlap in another direction of the Brillouin zone, and the relations between lattice spacings and composition become more complicated. The present paper describes an investigation of the lattice spacings of solid solutions

of lithium, magnesium, silicon, copper, zinc, germanium and silver in aluminium, this metal having been chosen as an example of a trivalent solvent with a face-centred cubic structure. The above solute elements are the only elements which dissolve in aluminium to an extent sufficiently great to permit an accurate lattice spacing/composition curve to be determined. The experimental methods and results are described in §§ 2 and 3 respectively, whilst in § 4 the theoretical implications of the results are described, and the validity of Vegard's law is discussed.

2. EXPERIMENTAL DETAILS

(a) *Metals used*

The *aluminium* used in the present work was super-purity metal supplied by the British Aluminium Co. Ltd., the certificate of analysis showed the following impurities:

Silicon	0.0015 %
Iron	0.0010 %
Magnesium	0.0010 %
Copper	0.0020 %
Aluminium (by difference)	99.9945 %

The *lithium* used was from a batch of specially pure metal presented by Professor R. S. Hutton. This metal has not been analyzed in the elementary state, but a series of magnesium-lithium alloys prepared from it gave no indication of impurities. The *copper* was of 99.995 % purity and was kindly presented by the British Non-Ferrous Metals Research Association. The *magnesium* was provided by the Ministry of Supply, and was of Dominion origin, the purity being of the order 99.97 %. The *silicon* was introduced in the form of a high-purity master alloy of aluminium and silicon which was supplied by the British Aluminium Co. Ltd. The *silver* was pure assay silver, and the *germanium* was specially purified metal, these two metals being supplied by Messrs Johnson Matthey and Co. Ltd. The *zinc* was kindly presented by the Imperial Smelting Corporation, and was of a purity exceeding 99.99 %.

(b) *Preparation and heat treatment of ingots*

The ingots used in the present work were prepared by melting the super-purity aluminium in crucibles lined with alumina-fluorspar mixture, using a standard flux, the solute metal being introduced either in the elementary state, or in the form of a master alloy. After thorough stirring with an alumina rod, the alloy was cast into heavy copper moulds, to give cylindrical ingots $\frac{3}{8}$ in. in diameter. The ingots were placed in alumina collars in sealed evacuated hard glass tubes, and were annealed for periods of the order of 1 week at a temperature of approximately 500° C, after which they were quenched in iced water. A surface layer of about 1 mm. was removed on a lathe, and the remainder of the ingot was then used for the preparation of the filings.

(c) Preparation and heat treatment of filings

From 0.5 to 1.0 g. of filings were prepared from each ingot, using a dead-smooth file. The filings were cleaned with ether, using the methods described by Hume-Rothery & Reynolds (1936). The clean dry filings were then placed in thin alumina thermocouple sheaths in sealed evacuated glass tubes; in this way the filings were prevented from coming into contact with glass, and contamination by silicon was avoided.* The exact heat treatment given to the filings depended on the system concerned. For alloys lying within the range of the solid solution at low temperatures, the annealing treatment was followed by slow cooling. In many systems the limits of the solid solution under equilibrium conditions at low temperatures are so restricted that it was necessary to quench the filings after annealing at a temperature at which they were homogeneous. In some cases it was sufficient to cool the sealed glass tube in a blast of cold air, whilst in others more drastic quenching was necessary in order to retain the homogeneous solid solution. In all such cases the results were examined carefully to ensure that the measured lattice spacings referred to the true homogeneous state, and not to a partly decomposed specimen. After quenching, the filings were washed with alcohol and ether, and were dried in a vacuum. The dried filings were then passed through an 80-mesh sieve in order to remove broken glass, and any unduly large metallic particles.

(d) Preparation of X-ray specimen and analysis of filings

In the present work no results were obtained which suggested that the filings were of uneven composition, but the possibility of slight transverse segregation† in the ingots could not be avoided, and it was therefore desirable to carry out the chemical analyses on samples which were as nearly as possible identical with those of the X-ray specimen. For this reason the material which had passed the 80-mesh sieve was used both for the preparation of the X-ray specimen and for the chemical analysis. Experiment has shown that the use of a finer sieve has very little effect on measurements of lattice spacing, and it is felt that for the present purpose the increased accuracy in the analysis‡ outweighs any advantage which might be gained by the use of a finer sieve.

The X-ray specimens were made by mixing a small portion of the filings with a solution of Canada balsam in xylol until a pasty mass was obtained. The paste was then rolled into thin cylinders of diameter about 0.4 mm., and after these had been dried they were mounted in the X-ray camera.

The chemical analyses of the specimens were carried out by Messrs Johnson Matthey and Co. Ltd., and the authors must express their thanks to Mr A. R. Powell for his care and attention. In a few cases particles of glass were found mixed with the

* Experiment has shown that aluminium filings pick up silicon when annealed in glass tubes.

† Experience with many polyphase aluminium alloys has shown that slight transverse segregation is often present in chill castings.

‡ It will be appreciated that if a very fine sieve is used, either the chemical analysis has to be carried out on a very small sample, or, alternatively, a much larger sample of metal has to be filed up, in which case the possibility of uneven composition is increased.

filings, and were weighed separately. All alloys were then analyzed for both constituents, and no indication of contamination was found. The work was straightforward except for the aluminium-germanium alloys for which very low results were at first obtained for the germanium. This source of error was eventually traced to the escape of germanium in the form of hydride, and the difficulty was avoided by dissolving the alloy in a mixture of nitric and sulphuric acids.

(e) *X-ray technique and lattice-spacing measurements*

The Debye-Scherrer photographs were taken in a 19 cm. diameter Unicam camera, using unfiltered copper radiation obtained from a Metro-Vickers demountable X-ray unit. With this radiation the pure aluminium gives (511), (422) and (420) reflexions at angles of 82, 69 and 58° respectively. The films were all of good quality, and could be measured accurately on a travelling microscope which had been tested against a standard scale calibrated at the National Physical Laboratory. The lattice spacings were calculated by standard methods, using the extrapolation function of Nelson & Riley (1945). During an exposure the temperature was measured by means of a thermometer placed on the camera, and for convenience all lattice spacings were calculated for a standard temperature of 25° C. For this purpose the coefficient of linear expansion was assumed to be 23.1×10^{-6} , the value for pure aluminium.*

The values given for the lattice spacings are in kX units, and have not been corrected for refractive index. This policy has been adopted in order to make the data directly comparable with those of most other authors.

3. EXPERIMENTAL RESULTS

(a) *Pure aluminium*

In the course of the present work nine determinations of the lattice spacing of pure aluminium were made, involving the preparation of five completely different samples of filings. The measured lattice spacings, reduced to 25° C, lay within the extremes 4.0412(8) and 4.0414(2) kX, with a mean value of 4.0413(4) kX at 25° C. This value is in good agreement with the values† 4.0413(6) kX of Jette & Foote (1935), and 4.0413(1) kX of Wilson (1941), and is within 0.0002 kX of the work of several other investigators.

(b) *Solid solutions of lithium, silicon, copper and zinc in aluminium*

The lattice spacings obtained in the course of the present work are given in table 1, and the relations between lattice spacings and composition are shown in figures 1 and 2. All these elements‡ produce a lattice contraction, and the following points may be noted.

* Experimental work has shown that the differences between the coefficients of expansion of the various alloys produces a negligible effect when the correction is for 10° C or less.

† In comparing the different papers care must be taken to see whether the correction for refractive index has been applied.

‡ The data for the aluminium-lithium alloys are included in figure 2 to avoid overlapping of points in figure 1.

TABLE I

The table contains the measured lattice spacings of the aluminium-rich solid solutions which have been investigated. All values have been corrected to 25° C.

solute element	weight % solute	atomic % solute	lattice spacing at 25° C kX
Li	0.91	3.44	4.0396(7)
	1.29	4.83	4.0392(7)
	1.93	7.11	4.0381(9)
Mg	0.31	0.35	4.0422(1)
	0.57	0.63	4.0428(6)
	0.73	0.81	4.0435(7)
	1.13	1.26	4.0458(3)
	2.14	2.37	4.0495(7)
	2.69	2.97	4.0511(2)
	3.17	3.50	4.0543(6)
	3.72	4.11	4.0563(9)
	5.06	5.58	4.0630(6)
	6.14	6.76	4.0688(7)
	8.86	9.73	4.0820(9)
	9.62	10.56	4.0860(8)
Si	0.24	0.23	4.0408(1)
	0.36	0.35	4.0406(5)
	0.70	0.67	4.0402(1)
	0.77	0.74	4.0400(4)
	0.81	0.78	4.0399(0)
	0.95	0.91	4.0397(3)
	0.96	0.92	4.0396(4)
	0.97	0.93	4.0396(0)
Cu	0.11	0.06	4.0411(7)
	0.93	0.40	4.0394(0)
	1.82	0.80	4.0372(1)
	2.88	1.23	4.0353(9)
	3.12	1.37	4.0347(8)
	3.71	1.62	4.0335(5)
Zn	1.05	0.43(6)	4.0412(2)
	4.09	1.70	4.0403(8)
	6.45	2.76	4.0396(7)
	6.78	2.91	4.0393(5)
	12.24	5.44	4.0373(3)
	13.33	5.96	4.0369(6)
	14.88	6.72	4.0360(5)
Ge	1.0	0.37	4.0418(8)
	2.34	0.88	4.0426(0)
	2.99	1.13	4.0431(1)
	3.68	1.40	4.0434(7)
	4.85	1.86	4.0444(8)
Ag	5.06	1.98	4.0446(5)
	10.0	2.7	4.0413(3)
	20.0	6.0	4.0413(6)
Pure aluminium of 99.9945 % purity			4.0413(4)

In the system *aluminium-zinc* (figure 1) the lattice-spacing composition relation is not linear, but is a curve such that the lattice contraction per atomic per cent of solute increases with the concentration. The points lie well on a smooth curve with

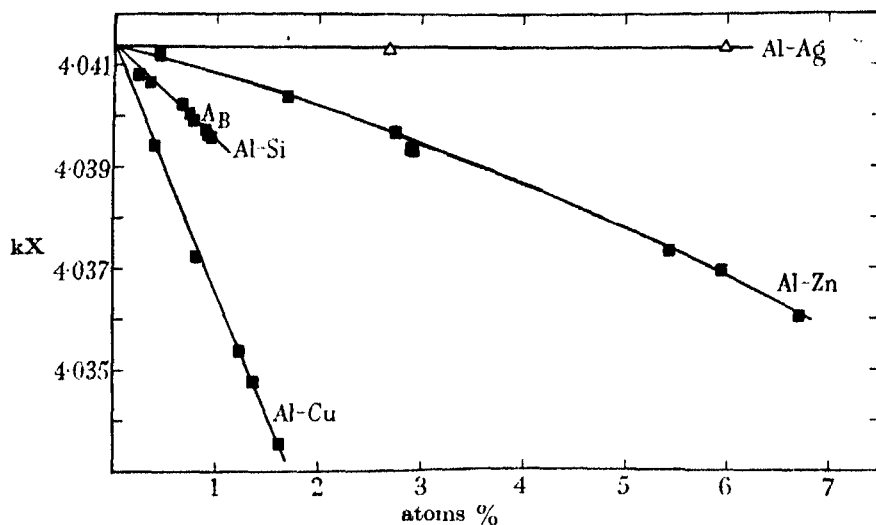


FIGURE 1

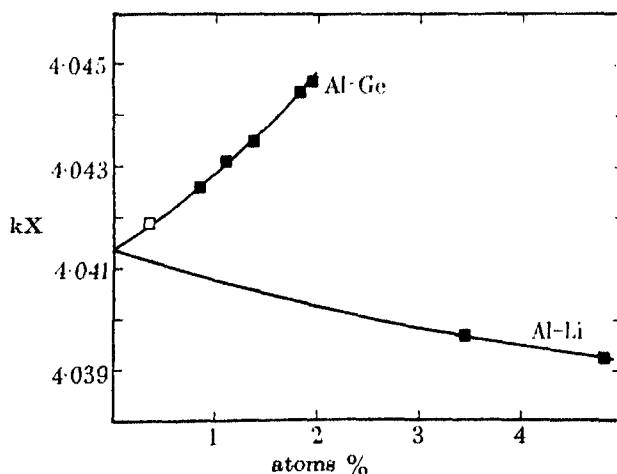


FIGURE 2

one exception, for which the divergence is 0.0002 kX. In the system *aluminium-copper* the lattice spacing/composition relation is linear. One point lies slightly below the best straight line, but the difference is within the limits of the experimental accuracy. In the system *aluminium-silicon*, a straight line can be drawn through all the points within the limits of experimental accuracy. In this system the solid solution is restricted, and experiments were made with two different rates of quenching, in order to ensure that partial decomposition had not occurred. The

points marked *A* and *B* were obtained in this way, and their good agreement suggests that the solid solution had been retained. In the system *aluminium-lithium*, the previous work of Zintl & Woltersdorf (1935) suggested that the lattice of aluminium was expanded by the solution of lithium, whereas the data of Vosskuhler (1937) indicated a contraction. The present work confirms that a contraction of the lattice takes place, and as will be seen from figure 2, the lattice spacing/composition line is slightly curved.

(c) *Solid solutions of magnesium, germanium and silver in aluminium*

The lattice spacing of aluminium is expanded considerably by the solution of magnesium and germanium, and is unaltered by silver. The results obtained are given in table 1, and are shown in figures 1, 2 and 3.

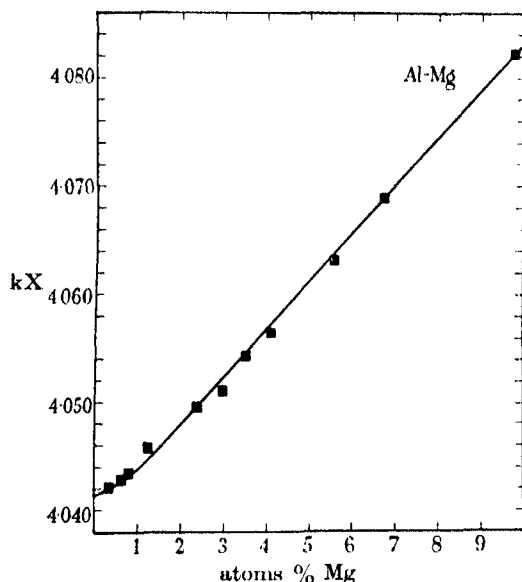


FIGURE 3

In the system *aluminium-magnesium*, the limits of the aluminium-rich solid solution are approximately 16 atomic % magnesium at 450° C, and 3 atomic % magnesium at 200° C. It was found that decomposition during quenching was effectively prevented by cooling in a blast of air. As will be seen from figure 3, ten of the twelve observed points lie on a curve which, after 2 atomic % magnesium, is practically a straight line, but which shows a definite curvature at the lower percentages. The two remaining points lie above and below this line by amounts of the order 0.001 Å which is equivalent to 0.25 % on the composition axis. It is thought that most of this discrepancy is due to the analyses rather than to the lattice-spacing measurements, because the films were of good quality and could be measured well. A great deal of attention was given to the question of the curvature

at low percentages of magnesium. The form of the lattice/spacing composition curve naturally suggests the presence of an impurity which is removed on alloying, but it would be necessary to assume a value of 4.0404 kX for the lattice spacing of the solvent metal in order to produce a lattice spacing/composition curve which was free from abnormal curvature at low percentages of magnesium. This would be in contradiction to the results of all previous investigators, and would also lead to improbable curvatures in the lattice spacing/composition curves for the other alloys investigated, unless it were assumed that the hypothetical impurity remained constant in these. No convincing explanation based on errors in analysis could be found to explain the abnormal curvature, and in general the synthetic and analyzed composition of the specimens were in good agreement. It seems, therefore, that additions of less than 1 atomic % of magnesium produce a slightly smaller expansion in the lattice as compared with the effect of larger percentages. The present results are in very good agreement with two points obtained for 6.61 and 9.01 atomic % magnesium by Brick, Phillips & Smith (1935), who showed that the use of quenched rods gave erroneous values owing to the straining of the specimen, although quenched filings gave accurate results; unfortunately, these investigators did not examine alloys with lower percentages of magnesium.

In the system *aluminium-germanium*, the lattice spacing/composition relation is very slightly curved, and as will be seen from figure 2 the experimental points are quite consistent. As explained on p. 4 the analyses of these filings gave rise to difficulties, and much additional work had to be carried out before the problem was solved. As a result of this work it was shown that the intended compositions of these alloys were attained to a high degree of precision, and the point marked with an open square which refers to an unanalyzed specimen has therefore been included.

In the system *aluminium-silver* the addition of 6 atomic % of silver produces no measurable change in the lattice spacing of silver. Only two alloys have been analyzed, and the points for these are shown in figure 1, but three measurements were also made for other alloys. The results confirmed that no detectable change in lattice spacing could be observed. The microstructures of the annealed and quenched alloys were therefore examined, and were found to indicate a homogeneous solid solution. The constancy of the lattice spacing appears therefore to be a genuine characteristic of the solid solution, and does not indicate a negligibly small solid solubility of silver in aluminium. This was confirmed by the absence of extra lines on the X-ray films.

4. DISCUSSION

(a) *The apparent atomic diameters*

The results described in § 3 show clearly that the lattice spacing of aluminium is expanded by the solution of magnesium and germanium, and contracted by the solution of lithium, silicon, copper and zinc. In the alloys with silicon, copper and silver the lattice spacing/composition curves are straight lines, and if these are extrapolated to 100 atomic % of solute we obtain what may be called the apparent

lattice spacings a of the solute in a hypothetical face-centred cubic structure, and the corresponding *apparent atomic diameters* are equal to $\frac{1}{2}(a\sqrt{2})$; we shall use the abbreviation A.A.D. for this quantity. In the alloys with lithium and zinc, the lattice spacing/composition curves are not exactly straight lines, but the curvature is so slight that tangents can easily be drawn to the curves at zero concentration of the solute, and the corresponding A.A.D. values can be obtained. In the alloys with magnesium, the abnormal curvatures referred to on p. 8 makes the above treatment less certain, and we have therefore estimated two A.A.D. values, one referring to the curve at zero concentration, and the other to the almost linear portion of the curve.

In this way the A.A.D. values for the above elements, when dissolved in aluminium, can be obtained, and existing data enable us to deduce the corresponding A.A.D. values for Al, Si, Zn, Ge and Ag when dissolved in copper, and for Mg, Al, Cu, Zn and Ge when dissolved in silver, and for Al, Cu, Zn and Ge when dissolved in gold. Since copper, silver and gold are univalent solvents the first Brillouin zone is only half filled, and the A.A.D. values deduced from the lattice spacings of dilute solutions are therefore free from any complications resulting from B.Z.* effects, and refer to a crystal structure (face-centred cubic) which is the same as that of aluminium. For solid solutions in magnesium the variation of the a -spacing with composition enables A.A.D. values to be obtained for lithium, aluminium and silver. These refer to a condition after a B.Z. overlap,† and since the crystal structure is normal close-packed hexagonal ($c/a = 1.6235$), the co-ordination number is 12 as in the face-centred cubic structure. For abbreviation we use the symbol a to denote the distance between an atom and its six neighbours in the basal plane, and the symbol d for the distance between an atom and its six other close neighbours, three in the layer above and three in the layer below. In the ideal case where the axial ratio equals $\sqrt{\frac{3}{2}}$, a and d are equal.

The above procedure enables us to compare A.A.D. values of the elements concerned when in dilute solid solution in univalent copper, silver and gold, divalent magnesium and trivalent aluminium. All these solvents crystallize with structures of co-ordination number 12, and so far as the crystal structures of the solvents are concerned, the conditions for comparison are favourable, and comparison may also be made directly with the atomic diameter (A.D.) values (i.e. the closest distances of approach) in the crystals in the elements aluminium, magnesium, copper, silver and gold.

Lithium crystallizes in the body-centred cubic structure of co-ordination number 8, whilst silicon and germanium crystallize in the diamond type of structure of co-ordination number 4, and it is clear that the different co-ordination numbers introduce a further complication in comparing the A.D. and A.A.D. values. According

* For abbreviation the letters B.Z. are used for Brillouin zone.

† The variation of c -spacing in solid solution in magnesium cannot be used to calculate A.A.D. values because as little as 1 atomic % of a trivalent element causes a new B.Z. overlap in this direction (see Hume-Rothery & Raynor 1940; Raynor 1942).

to Goldschmidt contractions of 4 and 12 % result from changes of co-ordination number $12 \rightarrow 8$ and $12 \rightarrow 4$ respectively. Examination of the original Goldschmidt papers (1928) shows that many of the so-called Goldschmidt atomic diameters were obtained from X-ray crystal data for metallic phases which are now known to involve B.Z. overlaps, so that the whole position is much more complicated than was originally imagined (see p. 15). The above contractions of 4 and 12 % must therefore be regarded only as giving a rough indication of the magnitudes involved, and for this reason we have not tabulated values of the Goldschmidt atomic diameters, although we shall refer to these occasionally. The data obtained are summarized in table 2 which also gives the A.A.D. values of gallium, cadmium, indium and tin referred to later. Examination of table 2 will show that for the solid solutions in aluminium the following principles are apparent:

(a) The tetravalent elements silicon and germanium when in solid solution in aluminium give A.A.D. values greater than those for solid solutions of the same elements in univalent solvents, and greater than the A.D. values. The effect is so marked that the A.A.D. values would be greater than the A.D. values increased by 12 %, i.e. greater than the Goldschmidt atomic diameters.

(b) The univalent elements lithium, copper and silver when in solid solution in aluminium give A.A.D. values smaller than those for solid solutions in univalent elements, and smaller than the A.D. values; this effect is particularly marked for lithium.

TABLE 2

solvent	solutes											
	Li	Mg	Al	Si	Cu	Zn	Ga	Ge	Ag	Cd	In	Sn
copper	—	—	2.71	2.59	—	2.70	2.75	2.78	2.95	3.10	3.20	3.26
silver	—	2.94 to 2.95	2.97	—	2.63	2.75	2.83	2.90	—	3.03	3.10	3.18
gold	—	—	2.80	—	2.63	2.74	2.83	2.93	—	3.00	3.07	3.14
magnesium	$a = 3.11$	—	2.81	—	—	—	2.83	—	2.64	3.00	3.08	3.13
	$d = 3.00$	—	2.85	—	—	—	—	—	2.53	—	3.16	—
aluminium	2.82	3.15 or 3.04	—	2.73	2.51	2.85	—	2.96 or 2.98*	2.86	—	—	—
interatomic distances in element	3.03	3.19	2.86	2.35	2.55	$a = 2.66$ $d = 2.90$	—	2.44	2.88	—	—	—
co-ordination number in element	8	12	12	4	12	6	—	4	12	—	—	—

Table 2 shows A.A.D. values for solid solutions of

Al, Si, Zn, Ge, Ag, Ga, Cd, In and Sn in copper,
Mg, Al, Cu, Zn, Ge, Ga, Cd, In and Sn in silver,
Al, Cu, Zn, Ge, Ga, Cd, In and Sn in gold,
Li, Al, Ag, Ga, In and Sn in magnesium,
Li, Mg, Si, Cu, Zn, Ge and Ag in aluminium,

together with values for the interatomic distances in elemental crystals of Li, Mg, Al, Si, Cu, Zn, Ge and Ag.

* The two estimates for the A.A.D. value of Ge in Al arise from the curvature of the lattice spacing/composition curve in a manner similar to that already discussed for the solution of Mg in Al.

(c) The divalent elements magnesium and zinc when dissolved in aluminium give A.A.D. values which are slightly larger than those for solid solutions in univalent elements. The A.A.D. values from solutions in aluminium are smaller than the distances of approach in the crystals of zinc ($d = 2.907 \text{ kX}$) and magnesium ($d = 3.20 \text{ kX}$) in the direction of the main B.Z. overlaps. The A.A.D. value of zinc from solution in aluminium (2.85 kX) is larger than the a distance of approach in the crystal of zinc (2.66 kX); and this point is discussed later.

(b) Vegard's law

According to Vegard's law (1928) the lattice spacing/composition curve for a solvent and solute of the same crystal structure is a straight line joining the values for the two pure metals, and a similar relation with a correction for effects of co-ordination number exists for the A.D. values when the two metals have different structures. This law was originally (1921) advanced for salts in which oppositely charged ions are drawn together by Coulomb forces until their electron clouds overlap and produce intense repulsive forces which balance the attraction. It was later (1928) extended to metals, and although it is now recognized that many exceptionists exist, there is still a general tendency (cf. Huang 1947) to regard Vegard's law as a valid approximation. It appears to us that this view is incorrect, and that in a metal where the attractive forces are due to the electron gas, it is only in exceptional circumstances that we shall expect Vegard's law to hold. We may illustrate the principles involved by considering the solid solution of lithium in aluminium. Lithium itself crystallizes in the body-centred cubic structure with $a = 3.50 \text{ kX}$, and A.D. $= 3.03 \text{ kX}$. The Li^+ ion is very small compared with the closest distance of approach between two lithium atoms, so that the ions play a negligible part in determining the interatomic distances. The volume per valency electron, for which we may use the symbol V_e^* , is $21.5 (\text{kX})^3$, so that the electron gas of the valency electrons is very dilute. The detailed calculations of Bardeen (1938) show that the electron density of the valency electrons is reasonably constant over a large fraction of the total volume, and that it is only near to the ions that the nodes, etc., of the wave function produce marked variations in the valency electron density. The metal has a high compressibility ($K = 8.9 \times 10^{12} \text{ dynes/cm.}^2$) which is due mainly to the valency electrons, and only affected very slightly by the extremely small ionic overlap. We may therefore regard the crystal of metallic lithium as consisting of small Li^+ ions swimming in a very dilute valency electron gas, which is responsible both for the attraction holding the structure together, and for the repulsion which gives rise to the resistance to compression. As the attractive forces are due to the electron gas as a whole we cannot think of directed forces between adjacent atoms, but we may perhaps represent the relations involved by a model such as that of figure 4. In this figure the different atoms are represented by squares

* For abbreviation we shall omit the units $(\text{kX})^3$ in referring to the V_e values of different elements.

held together by very weak springs,* V_a representing the weak attraction of the dilute valency electron gas, and held apart by the very weak springs V_r representing the repulsion due to the valency electron gas. The much stronger springs I_r represent the repulsion of the electron clouds of the ions which is not yet effective because of the large interatomic distances. The interatomic distance 3.03 kX in lithium refers to a body-centred cubic structure, but the general condition of affairs would be the same in a hypothetical face-centred cubic structure, for which Goldschmidt's co-ordination factors would give an interatomic distance of 3.12 kX.

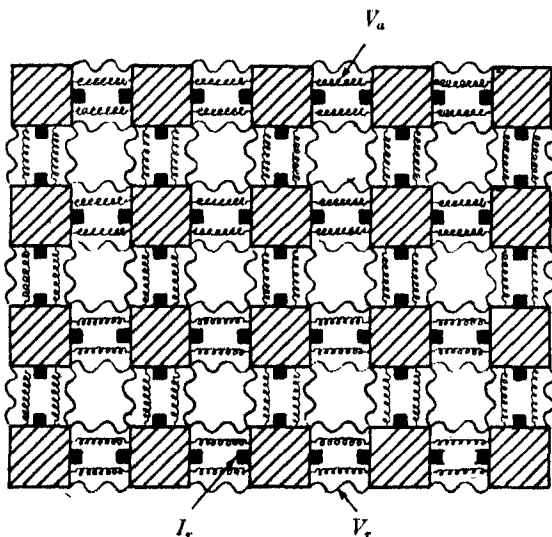


FIGURE 4

In the face-centred cubic structure of aluminium A.D. = 2.86 kX and the atoms are closer together than in lithium. There are now three valency electrons per atom, and $V_e = 5.51$, so that the valency electron gas is on the average about four times as concentrated in aluminium as in lithium. This concentrated electron gas is also less uniformly distributed than the dilute electron gas in lithium or sodium. As we proceed along the series $\text{Na} \rightarrow \text{Mg} \rightarrow \text{Al}$, the V_e values become progressively smaller, and the valency electron densities progressively greater, and at the same time the valency electrons tend to be more concentrated near to the ions. The melting-point of aluminium (659° C) is much higher than that of lithium (152° C), whilst its compressibility is much lower ($K = 1.37 \times 10^{12}$ dynes/cm.²). The attractive and repulsive forces are thus much stronger in aluminium, and are due mainly to the valency electrons, for the Al^{+++} ionic radii are smaller than the distances between the atoms in metallic aluminium, although the ionic overlap is greater than in an alkali metal. We may therefore represent the condition of affairs in aluminium by a diagram such as that of figure 5, where the valency attractive springs V_a and repulsive springs V_r

* The springs will be non-linear and will not obey Hooke's law.

are much stronger than the corresponding springs in figure 4 for lithium, and the ionic repulsion springs are more nearly touching.

We can now readily understand why the A.A.D. of lithium (2.82 kX) when dissolved in aluminium is so much smaller than the A.D. value (3.03 kX). For the A.D. value of 3.03 kX refers to the equilibrium of the very weak forces represented by the weak springs of figure 4, but when one of these atoms is substituted for an aluminium atom, the much stronger forces of the aluminium lattice, represented by the stronger springs of figure 5, will cause an almost complete collapse of the weak springs. In this connexion there is a difference between the behaviour of a 1-dimensional row, and a 2- or 3-dimensional lattice. In a 1-dimensional row, a single atom could exert its own influence, but in 2- or 3-dimensional lattices a distortion round one atom affects the interatomic distances between other atoms. We can therefore understand why the A.A.D. (2.82 kX) of lithium when dissolved in aluminium is nearly the same as the A.D. of aluminium itself (2.86 kX), and since the ion of lithium is smaller than the ion of aluminium we can perhaps also understand why the A.A.D. of lithium in aluminium is slightly smaller than 2.86 kX.

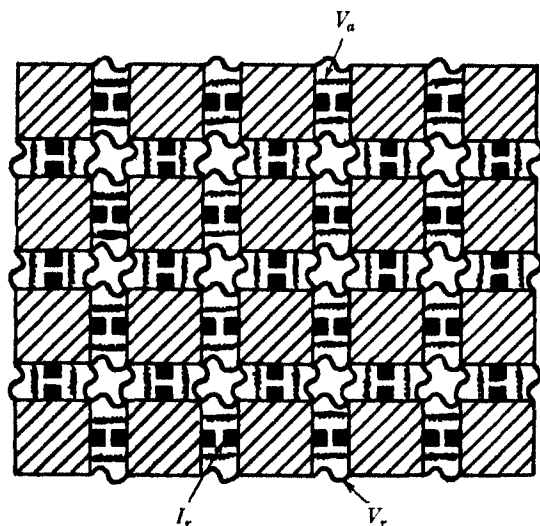


FIGURE 5

If the above line of argument be accepted, it will be realized that it is only in exceptional cases that the so-called Vegard's law can be expected to hold for metals. So far as we have been able to discover, the system calcium-strontium is the only alloy system in which a linear relation holds between the lattice spacing and atomic percentages of the two metals. It is perhaps significant that in this case the V_a value for strontium is larger than that for calcium, whilst its ionic radius is also larger. When strontium is dissolved in calcium we expect the valency electron effect to produce a smaller A.A.D. for the same reason as that described above for lithium in aluminium, but the larger ion of strontium may produce a counterbalancing expansion.

(c) *Factors controlling the apparent atomic diameters*

The exact A.A.D. values of one metal in different solvents will clearly depend on the exact details of the atomic fields and cannot be predicted, but we suggest that a general interpretation may be obtained by considering the following controlling factors.

(1) *The V_e effect*

In the above description we have seen why the A.A.D. of lithium when dissolved in aluminium is so much smaller than the A.D. for metallic lithium. In this case the V_e values for lithium and aluminium are 21.7 and 5.5 respectively. The V_e values for the remaining elements are given in table 3, and we suggest that as a first approximation these may be used to indicate the direction of effects analogous to those described for lithium and aluminium. That is to say, if the V_e value of the solute is greater than that of the solvent, we expect the A.A.D. to be made smaller, and, conversely, if the V_e of the solvent is larger than that of the solute we expect the A.A.D. to be made larger. This simple effect may then be obscured by the complicating factors described below.

TABLE 3

element	V_e for co-ordination no. 12	element	V_e for co-ordination no. 12
Li	21.7	Ga	c. 6-7
Cu	11.7	In	c. 8-9
Ag, Au	17.0	Si	3.2
Mg	11.6	Ge	3.6
Zn	6.7	Sn	5.6 grey tin
Cd	9.0		5.5 white tin
Al	5.51		

(2) *The effect of ionic radius*

We suggest that if the ionic radius of the solute is larger than that of the solvent, the effect is to increase the A.A.D. of the former, and, conversely, if the ionic radius of the solute is the smaller, its A.A.D. tends to be smaller. This effect is, however, only marked if a relatively large ion is being forced into a structure in which its electron cloud begins to overlap the electron cloud of the *ions* of the solvent, e.g. when silver is dissolved in copper. Figure 6 shows the univalent ionic radii of the elements concerned, and these may be taken (Hume-Rothery & Raynor 1940) as the least unsatisfactory values if the 'size' of an ion is to be represented by a single number; they must not, of course, be taken to indicate a sharp boundary surface to the ion. Thus in metallic copper, the electron clouds of the ions overlap appreciably, and are responsible for the low compressibility, although the univalent radius of the Cu^+ ion is only 0.96 kX as compared with a half distance of approach of 1.27 kX. It has also been emphasized (Hume-Rothery & Raynor 1938) that in the elements following an alkali metal (e.g. $\text{Na} \rightarrow \text{Mg} \rightarrow \text{Al} \rightarrow \text{Si}$) the electron clouds of the ions shrink less rapidly than the interatomic distances, so that the crystal structures

become less 'open' with increasing valency, whereas in the elements following copper, silver and gold (e.g. $\text{Cu} \rightarrow \text{Zn} \rightarrow \text{Ga} \rightarrow \text{Ge}$) the ion shrinks the more rapidly and the structures become increasingly more open.

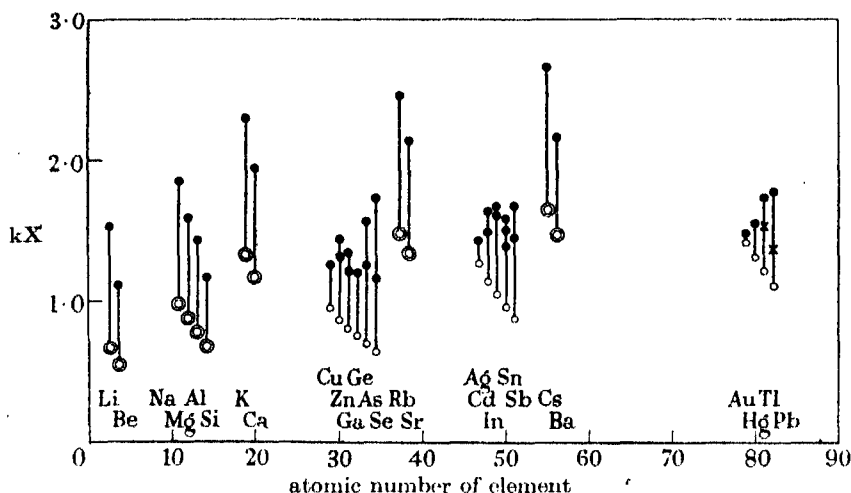


FIGURE 6. Atomic and ionic radii of the elements. (Reproduced from *Phil. Mag.* 1938, 26, 136.) ● $\frac{1}{2}$ (interatomic distance in the crystal of the element). ○ Zachariasen univalent ionic radii. ○ Pauling univalent ionic radii. × Goldschmidt empirical ionic radii.

(3) The effects of Brillouin zone overlaps

It has been shown by Jones (1934) that the effect of a B.Z. overlap is to produce an expansion of the crystal in the direction concerned. Hume-Rothery & Raynor (1940) and Raynor (1942) have shown that when 3- and 4-valent elements are dissolved in magnesium, the lattice spacing/composition curves for the a -spacings are smooth, whilst those for the c -spacings show a kink in the direction of an expansion after a small percentage of solute (see figure 7). This was taken to imply that in pure magnesium a B.Z. overlap had already occurred in the a direction, but not in the c direction, although the latter overlap occurred after a very slight increase in the electron concentration. Hume-Rothery & Raynor suggested that the A.D. in aluminium (2.86 kX) was greater than its A.A.D. when dissolved in copper (2.71 kX) and silver or gold (2.79–2.80 kX), because no B.Z. overlap was concerned in the univalent solutes. From table 2 it is clear that the position is not really so simple: thus the A.A.D. value for indium dissolved in magnesium (3.08 kX) is almost the same as the values (3.07, 3.11 kX) for solutions in gold and silver,* whilst the A.A.D. value for gallium dissolved in magnesium (2.83 kX) is smaller than those (2.835, 2.838 kX) for solutions in silver and gold. It is, of course, clear that with a lattice spacing/composition curve such as that of figure 7, extrapolation of the curve immediately after the overlap will give a higher A.A.D. for the element of higher

* The solid solution of indium in copper is affected by the overlapping of the ions as described below.

valency than the A.A.D. obtained by extrapolation of the curve immediately before the overlap, and similarly extrapolation of a curve after an overlap will give a lower A.A.D. value for the element of lower valency. If we consider a continually increasing electron concentration, it seems probable that the expansion produced by each successive B.Z. overlap will remain at higher electron concentrations, but the effects of sharp peaks and valleys in the $N(E)$ curve on the lattice spacings cannot be predicted without further details. We may therefore expect a general tendency for a B.Z. overlap to produce an expansion, and for increasing and decreasing electron concentration immediately after an overlap to produce large and small A.A.D. values respectively, but the results are more complicated than those imagined previously.

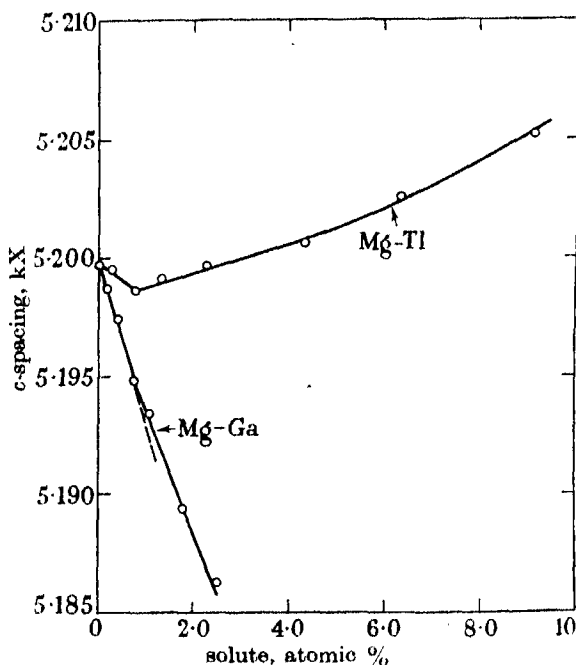


FIGURE 7

When we consider the lattice spacing/composition curves for 3- and 4-valent solutes in magnesium, extrapolation of the a -spacing curve, and of the c -spacing curve *after the kink*, will give us a and c values for a hypothetical structure with B.Z. overlaps in both a and c directions, and the corresponding A.A.D. values can be calculated for the a and d distances of approach. The c -spacing curve before the kink is too short for extrapolation. In contrast to this if we consider the corresponding curves for a *univalent* metal dissolved in magnesium, extrapolation will give us a and c values for a structure with no overlap in the c direction.

In the earlier papers of Hume-Rothery & Raynor it was assumed that the condition of affairs in aluminium was one following after the (200) B.Z. overlap of the face-centred cubic structure, since this was what was indicated by the simple B.Z.

theory of Mott & Jones (1937). It has lately been shown by Matyas* that the symmetry of the s and p states results in an $N(E)$ curve of the type shown in figure 8 in which, although the first zone is very nearly filled, the (200) overlap has not taken place. The unoccupied states in the first zone lie in thin slabs parallel to the (200) faces of the zone. This condition of affairs is quite different from that of the simple theory of electrons in the face-centred cubic structure, according to which the occupied states would have reached to, and spread out from, the centres of the (200) faces.

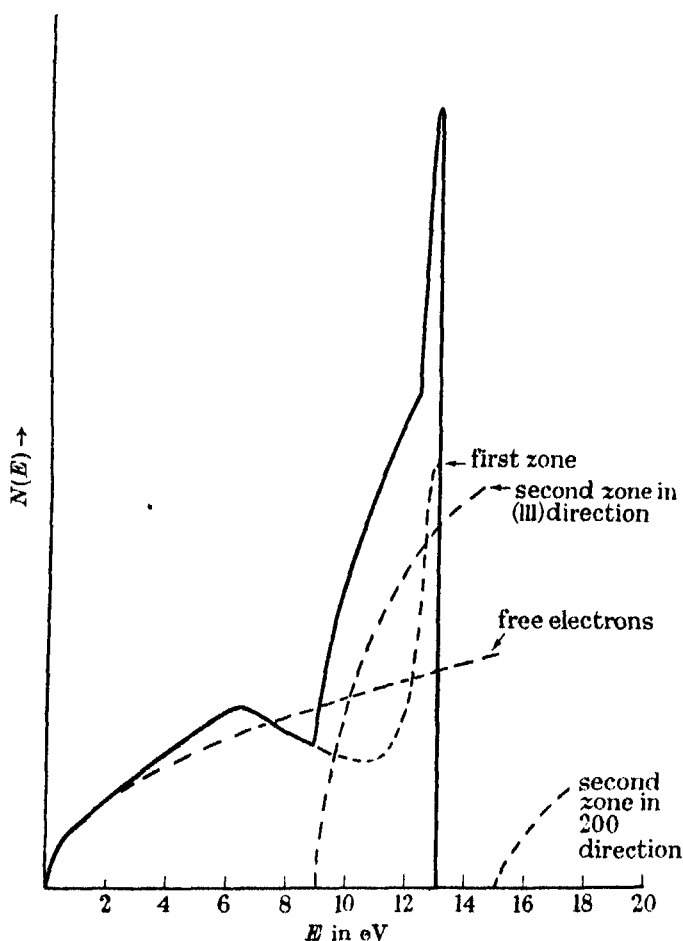


FIGURE 8

The new $N(E)$ curve is of very great interest, and offers one explanation of the scarcity of elements which form wide solid solutions in aluminium. For with elements of both higher and lower valencies, the formation of an appreciable solid solution would alter the electron concentration so that the latter corresponded to

* We have to thank Dr Matyas for allowing us to use these results.

a lower position on the $N(E)$ curve, and hence to a structure which became relatively less stable compared with other possible structures whose $N(E)$ curves remained high. Actually the various equilibrium diagrams suggest that at low temperatures no element forms an appreciable solid solution in aluminium, whilst at high temperatures zinc is the only element whose solubility exceeds 20 atomic %. The complete absence of any solid solutions at low temperatures is not explained by the above $N(E)$ curve, since with a slight solid solution the electron concentration would still correspond to a relatively high position on the $N(E)$ curve. There is also no obvious reason why the trivalent elements gallium and indium do not form wide solid solutions in aluminium, and the explanation of this must presumably lie in the details of the atomic fields, as distinct from simple electron concentration effects.

The $N(E)$ curve of Matyas shows that in pure aluminium there will be slightly more than one electron per atom in the states of the second zone, and the Fermi surface will lie well beyond the point at which the (111) overlap begins. So far as B.Z. effects are concerned, we shall therefore expect the aluminium lattice to be expanded by the (111) overlap,* but in aluminium-rich alloys we shall not be in the region of electron concentration immediately following an overlap.

(4) *The effect of the electrochemical factor*

It has already (Hume-Rothery 1946) been suggested that when the solvent and solute differ markedly in the electrochemical series the effect is to introduce forces of a partly ionic nature, and we may expect this to produce a contraction of the lattice which will make the A.A.D. smaller.

(d) *Detailed examination of the apparent atomic diameters in different solvents*

If the preceding arguments are accepted we may expect the A.A.D. values to be determined by the interplay of (1) the V_e effect, (2) the effect of ionic radius, (3) the electrochemical factor and (4) B.Z. effects. These different factors may either reinforce or oppose one another, so that the whole problem is very complicated. No suggestion is made that the details can be predicted, but the following tentative interpretation of the figures in table 2 is offered as indicating that some of the principles have been correctly identified. For convenience we may divide the data under the following sub-headings.

Solid solutions in which the V_e effect tends to produce a small A.A.D. value

Of the systems concerned in table 4, the general tendency is clearly for the A.A.D. to be smaller than the A.D. An exception is presented by the solid solution of silver in copper, and this is the only case in which the formation of the solid solution involves the forcing of a larger ion into a structure which is already of the full type. This is therefore the system in which the effect of a larger ionic radius in producing an expansion is likely to be the greatest, and we can understand why the A.A.D. is 0.07 kX greater than the A.D.

* Hume-Rothery & Raynor argued on the assumption of both (111) and (200) overlaps.

For the solid solution of lithium in magnesium the A.A.D. values are $a = 3.11$, and $d = 3.00$ kX, as compared with an A.D. value 3.03 kX. This last value refers to a co-ordination number of 8, and if we use the Goldschmidt correction factor for change of co-ordination no. $12 \rightarrow 8$, the value for a hypothetical face-centred cubic modification of lithium would be 3.13 kX. The A.A.D. values for lithium dissolved in magnesium are thus smaller than the A.D. value when corrected for co-ordination number. The magnesium-lithium data are from work by Hofmann (1936), and the experimental errors probably give too large* A.A.D. values, so that the actual difference between the A.A.D. and corrected A.D. values may be greater than that given.

TABLE 4

solute and V_e	solvent and V_e	effect of ionic radius	A.A.D.	A.D.
Li 21.7	Al 5.5	contract	2.825	3.03
Li 21.7	Mg 11.6	contract	$a = 3.11$ $d = 3.00$	3.03
Cu 11.7	Al 5.5	expand	2.51	2.55
Ag 17.0	Al 5.5	expand	2.86	2.88
Ag 17.0	Mg 11.6	expand	$a = 2.64$ $d = 2.53$	2.88
Ag 17.0	Cu 11.7	large expansion: ionic overlap	2.95	2.88
Mg 11.6	Al 5.5	expand	3.04 or 3.15	$a = 3.19$ $d = 3.20$
Zn 6.7	Al 5.5	expand	2.85	$a = 2.66$ $d = 2.91$

For the solid solution of zinc in aluminium the V_e value of the solvent is only slightly less than that of the solute, so that we expect the V_e effect to be small. The effect of the ionic radius will also be small but tends to produce an expansion. The A.A.D. value of 2.85 kX lies between the two sets of interatomic distance in zinc, but the crystal structure of the latter is so abnormal that detailed comparison is hardly justified.†

Solid solutions of copper, zinc, cadmium, gallium, indium, germanium and tin in silver, copper and gold, and of copper in silver; in these systems the V_e effect tends to produce a large A.A.D.

The data for these systems are shown in table 5. For the solid solutions of zinc, gallium and germanium in copper, silver or gold, the V_e effect leads us to expect a large A.A.D., the expansion becoming greater with increasing valency. We can there-

* The lithium used contained sodium and potassium, which may cause an expansion of the magnesium lattice. Further, any oxidation of the specimens would tend to give too large a lattice spacing, and no precautions against this source of error are described.

† In zinc the main B.Z. overlap is in the c direction, and there is a second and smaller overlap in the basal plane. The main overlap expands the crystal in the direction of the c -axis, and the elastic constants are such that this specimen tends to contract the distances in the basal plane, by an effect analogous to that of the Poisson ratio. The value $a = 2.66$ kX is thus probably smaller than if no B.Z. overlaps had occurred.

fore understand why the A.A.D. values for a series such as (Cu $\rightarrow$ Zn $\rightarrow$ Ga $\rightarrow$ Ge) when dissolved in copper, silver or gold increases with the valency. Since the V_e of copper (11.7) is smaller than that of silver and gold (17.0), the V_e effect will tend to produce a greater expansion for solid solutions in the latter metals, and as will be seen from table 5 the A.A.D. values of zinc, gallium and germanium from solid solutions in silver and gold are uniformly greater than those from solid solutions in copper, so that the general interpretation is confirmed. The same explanation may be offered for the fact that when copper is dissolved in silver, the A.A.D. of copper (2.64 kX) is greater than the A.D. in copper itself (2.55 kX).

TABLE 5

solute and V_e	solvent and V_e	effect of ionic radius	A.A.D.	A.D.
Cu 11.7	Ag 17.0	contract	2.64	2.55
Cu 11.7	Au 17.0	contract	2.63	2.55
Zn 6.7	Cu 11.7	contract	2.70	$a = 2.66$ $d = 2.97$
Zn 6.7	Ag 17.0	contract	2.75	$a = 2.66$ $d = 2.97$
Zn 6.7	Au 17.0	contract	2.74	$a = 2.66$ $d = 2.97$
Ga c. 6	Cu 11.7	contract	2.75	abnormal structures with distances from 2.44 to 2.79 kX
Ga c. 6	Ag 17.0	contract	2.835	
Ga c. 6	Au 17.0	contract	2.84	
Ga c. 6	Mg 11.7	very slight	2.83	
Ge 3.6	Cu 11.7	contract	2.78	2.44
Ge 3.6	Ag 11.7	contract	2.90	2.44
Ge 3.6	Au 11.7	contract	2.93	2.44
Cd 9.0	Cu 11.7	large expansion: ionic overlap	3.10	$a = 2.97$ $d = 3.29$
Cd 9.0	Ag 17.0	contract	3.04	$a = 2.97$ $d = 3.29$
Cd 9.0	Au 17.0	contract	3.00	$a = 2.97$ $d = 3.29$
In c. 8	Cu 11.7	expand: ionic overlap	3.21	3.24 3.37
In 8	Ag 17.0	contract	3.11	see p. 21
In 8	Au 17.0	contract	3.07	see p. 21
In 8	Mg 11.6	expand	$a = 3.08$ $d = 3.16$	
Sn 5.5	Cu 11.7	expand: ionic	3.27	2.80 grey
Sn 5.5	Ag 17.0	contract	3.18	3.02 3.18
Sn 5.5	Au 17.0	contract	3.14	white —

Comparison with the interatomic distances in crystals of zinc, gallium and germanium is not so simple. The A.A.D. values of zinc when dissolved in copper, silver and gold are smaller than the distance of approach $d = 2.97$ kX in the crystal

of zinc, and this can be understood because the latter involves the main B.Z. overlap. The value $a = 2.66 \text{ kX}$ for the closest distance of approach in the basal plane is affected by the curious elastic properties of the zinc crystal, and can hardly be compared directly with any of the other values.*

In the complicated crystal structure of gallium, the distances of approach vary from 2.44 to 2.79 kX , and the V_c effect has produced the expected relatively large A.A.D. values. In germanium, the crystal structure is of the diamond type with A.D. 2.44 kX . The A.A.D. values for germanium when dissolved in copper, silver and gold vary from 2.78 to 2.93 kX , and are thus larger than the A.D. by more than the 12 %, which Goldschmidt postulated on the effect of a change in co-ordination number $12 \rightarrow 4$. The V_c principle is thus strikingly confirmed, particularly when it is remembered that the A.A.D. values from solutions in univalent solvents are not affected by B.Z. overlaps, whereas the A.D. value of 2.44 kX for germanium includes the effect of B.Z. overlapping.

For the solid solutions of silver, cadmium, indium and tin in copper, silver and gold, the effect of ionic radius is now different. The ions of cadmium, indium and tin are smaller than those of silver and gold, just as the ions of zinc, gallium and germanium are smaller than those of copper. The ions of cadmium, indium and tin are, however, larger than, or at least equal* to, the ions of copper, so that the formation of a solid solution in copper results in the insertion of a larger ion into an already full structure, and we suggest that it is for this reason that the A.A.D. values of cadmium, indium and tin, when dissolved in copper, are larger than when dissolved in silver or gold; the effect is the same as that for silver when dissolved in copper (see p. 18). If this interpretation is correct, the system silver-copper is of interest in that the large A.A.D. value of copper in silver is the result of the V_c effect, whilst the large A.A.D. value of silver in copper is due to the effect of ionic radius.

The relations between the A.A.D. values for cadmium in the univalent solvents, and the A.D. values in metallic cadmium are analogous to those described above for zinc. In the case of indium, the A.D. values ($d_1 = 3.24$, $d_2 = 3.37 \text{ kX}$) in the element are slightly greater than the A.A.D. values in the univalent solvents, and for solution in divalent magnesium. According to Raynor (1940a) this is due to the existence of incomplete ionization in the element. It was not, however, clear why the A.A.D. values of indium from solutions in univalent silver and gold (3.11 and 3.07 kX) were as large as the A.A.D. value ($a = 3.08$, $d = 3.16$) for solution in magnesium, for the latter refers to a position shortly after a B.Z. overlap, whereas the former does not. The data in table 5 show that the V_c effect is greater for the solutions in silver and gold, and so the large A.A.D. values are explained. The same explanation accounts for the fact that the A.A.D. value of gallium dissolved in silver or gold is as large as the A.A.D. values for the solution in magnesium. But when gallium is dissolved in copper ($V_c 11.7$) the solvent has almost exactly the same V_c as magnesium

* See footnote on p. 19.

† The solid solubilities of indium and tin in copper indicate that the effect of the ionic overlap is considerable (see Hume-Rothery 1946).

(V_e 11.6), and consequently the V_e effects are the same, and the A.A.D. for the solution in magnesium (2.83 kX) is larger than that for the solution in copper (2.75 kX) because of the effect of the B.Z. overlap in magnesium.*

When tin is dissolved in copper, silver or gold the V_e effect indicates an expansion, and the larger A.A.D. in copper is the result of the ionic radius of tin being of the same order as that of copper, but smaller than those of silver and gold. The A.A.D. values for the solution in silver and gold are considerably greater than the A.D. (2.80 kX) in grey tin, and slightly greater than this value corrected for the Goldschmidt co-ordination effect.

TABLE 6

solute and V_e		solvent and V_e	effect of ionic radius	A.A.D.	A.D.
Mg 11.6		Ag 17.0	contract	2.94	$a = 3.20$ $d = 3.19$
Al 5.5		Cu 11.7	contract	2.71	2.86
Al 5.5		Ag 17.0	contract	2.79	2.81
Al 5.5		Au 17.0	contract	2.80	2.86
Al 5.5		Mg 11.6	contract	$a = 2.81$ $d = 2.85$	2.86
Si 3.2		Cu 11.7	contract	2.60	2.35
Si 3.2		Al 5.5	contract	2.73	2.35
Ge 3.6		Al 5.5	?	2.97	2.44

Solid solutions of magnesium, aluminium and silicon not previously discussed

The data for these systems are shown in table 6, and the following interpretation may be offered.

When magnesium ($V_e = 11.6$) is dissolved in silver ($V_e = 17.0$) the V_e effect indicates an expansion, which will be opposed by the relatively strong electrochemical factor, and by the effect of ionic radius. The resulting A.A.D. refers to a solid solution in which there is no B.Z. overlap, and we can understand why the resulting value is smaller than the interatomic distances $a = 3.20$ kX, $d = 3.19$ kX in pure magnesium.

When aluminium is dissolved in copper, silver or gold, the V_e effect indicates an expansion which is greater for the solutions in silver and gold. We suggest that it is for this reason that the A.A.D. values in silver and gold (2.79 and 2.80 kX) are greater than that for aluminium in copper (2.71 kX). The ionic radius effect indicates an opposing tendency which is greater for the solutions in silver and gold, but since this is a contraction it is a relatively small effect. All these figures refer to A.A.D. values for a univalent solvent in which B.Z. complications are absent, and as pointed out by Hume-Rothery & Raynor (1940), it is for this reason that they are smaller than the A.D. of aluminium itself (2.86 kX) in which a B.Z. overlap has occurred.

* As explained above this condition of affairs does not apply to solutions of indium in copper and magnesium, because the solution in copper involves a greater increased ionic overlap.

When aluminium is dissolved in magnesium, the V_e effect indicates an expansion, and the ionic radius effect a slight contraction. The solution of aluminium in magnesium results in an increase in the electron concentration shortly after a B.Z. overlap, and we can understand why the A.A.D. values of $a = 2.81$, $d = 2.85$ are greater than the A.A.D. values in copper, silver and gold. Comparison with the A.D. in aluminium itself is clearly not simple, because both aluminium and magnesium involve B.Z. overlaps.

For the solid solutions of silicon in copper and aluminium the V_e effect indicates an expansion, which is opposed by the relatively small effect of ionic radius. The A.A.D. of silicon dissolved in copper is free from B.Z. overlap effects, and it may be for this reason that the value (2.60 kX) is smaller than the corresponding value (2.73 kX) for the solution in aluminium where the solvent has already been expanded by one B.Z. overlap. Both these values are much greater than the A.D. of silicon (2.35 kX) which refers to a crystal structure of co-ordination number 4. If this is increased to allow for the Goldschmidt change in co-ordination number, the resulting value is 2.66 kX. The A.A.D. value for the solution in aluminium is greater than this, so that a very considerable expansion has occurred. The A.A.D. value from the solution in copper is 0.06 kX less than the Goldschmidt value, and this may be because the value 2.35 kX for elementary silicon is itself expanded by a B.Z. overlap.*

When germanium is dissolved in aluminium the V_e effect produces an expansion, and the A.A.D. (2.97 kX) is greater than the A.D. (2.44 kX) and greater than the latter corrected by the Goldschmidt co-ordination factor. In this case, as with silicon, both aluminium and the A.D. of the solute involve B.Z. overlaps, and we can understand why the A.A.D. is large, and why it is larger than the corresponding values for solid solutions in copper, silver and gold which were dealt with above.

5. CONCLUSION

As emphasized before, no claim is made that the exact A.A.D. values can be predicted, but it does appear that the values from the different solid solutions given in table 2 can be understood satisfactorily by consideration of the four factors outlined in subsection (c) above. In particular, the influence of what we have called the V_e effect is very striking, and the systems in which it is not the controlling factor are clearly those in which overlapping ions, or Brillouin zone effects, are present.

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* Since silicon contains 4 valency electrons per atom there must be at least one B.Z. overlap.

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Matrices of integers associated with self-transformations of surfaces

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Let $\mathbf{c} = (c_1, \dots, c_r)$ be a set of curves forming a minimum base on a surface, which, under a self-transformation, $\mathcal{F}$, of the surface, transforms into a set $\mathcal{F}\mathbf{c}$ expressible by the equivalences $\mathcal{F}\mathbf{c} = \mathbf{T}\mathbf{c}$, where $\mathbf{T}$ is a square matrix of integers. Further, let the numbers of common points of pairs of the curves, c_i, c_j be written as a symmetrical square matrix $\mathbf{\Gamma}$. Then the matrix $\mathbf{T}$ satisfies the equation $\mathbf{T}\mathbf{T}' = \mathbf{\Gamma}$.

The significance of solutions of this equation for a given matrix $\mathbf{\Gamma}$ is discussed, and the following special surfaces are investigated:

§§4-7. Surfaces, in particular quartic surfaces, with only two base curves. Self-transformations of these depend on the solutions of the Pell equation $u^2 - kv^2 = 1$ (or 4).

§8. The quartic surface specialized only by being made to contain a twisted cubic curve. This surface has an involutory transformation determined by chords of the cubic, and has only one other rational curve on it, namely, the transform of the cubic. The appropriate Pell equation is $u^2 - 17v^2 = 4$.

§9. The quartic surface specialized only by being made to contain a line and a rational curve of order m to which the line is $(m-1)$ -secant (for $m=1$ the surface is made to contain two skew lines). The surface has two infinite sequences of self-transformations, expressible in terms of two transformations $\mathcal{A}$ and $\mathcal{S}$, namely, a sequence of involutory transformations $\mathcal{A}\mathcal{S}^n$, and a sequence of non-involutory transformations $\mathcal{S}^n$.

1. CURVES ON A SURFACE WITH SELF-TRANSFORMATIONS

For this investigation we suppose that a surface Ω has a birational self-transformation, $\mathcal{F}$, in which there are no singular elements on Ω . Much of the work could be applied to more general transformations, but the statement of the results is much simplified by making this assumption.

If $\{a, b\}$ denote the number of points common to two curves a, b on Ω , and $\mathcal{F}a$ is the transform of a , then

$$\{\mathcal{F}a, \mathcal{F}b\} = \{a, b\}.$$

Let the set of r curves $c_1, \dots, c_r$ on Ω form a minimum base in terms of which all other curves may be expressed by linear equivalences. Then, in particular, the curves $\mathcal{F}c_i$ may be so expressed, say

$$\mathcal{F}c_i = \sum t_{ij} c_j, \quad (1.1)$$

where the t_{ij} form a square matrix $\mathbf{T}$ of integers (positive, negative, or zero).

For the inverse transformation, $\mathcal{F}^{-1}$, we shall have also

$$\mathcal{F}^{-1}c_k = \sum T_{kl} c_l,$$

where

$$\sum t_{ij} T_{jl} = \delta_{il},$$

so that the matrix $\mathbf{T}$ is non-singular. If we regard the curves c_i collectively as the elements of a column vector $\mathbf{c}$, we may write (1.1) in the form

$$(\mathcal{F}\mathbf{c}) = \mathbf{T}\mathbf{c}. \quad (1.2)$$

Consider next the symmetrical matrix Γ formed by the numbers of intersections of pairs of the curves c_i , including either the number of intersections of each curve with another curve of the linear family defined by it, or, if the curve is unique, the number of virtual self-intersections, i.e.

$$\Gamma = \Gamma' = (\gamma_{ij}) = (\gamma_{ji}) = (\{c_i, c_j\}). \quad (1.3)$$

(We assume Γ to be non-singular.) Then

$$(\{\mathcal{T}c_i, c_k\}) = (\{\sum t_{ij}c_j, c_k\}) = (\sum t_{ij}\gamma_{jk}) = \mathbf{T}\Gamma$$

and

$$(\{\mathcal{T}c_i, c_k\}) = (\{c_i, \mathcal{T}^{-1}c_k\}) = (\sum t_{kj}\gamma_{ji}) = \Gamma(\mathbf{T}')^{-1},$$

so that

$$\mathbf{T}\mathbf{T}\mathbf{T}' = \Gamma. \quad (1.4)$$

Thus

1.1. If $\mathbf{c} = (c_i)$ is any minimum set of base curves on a surface Ω , and $\Gamma = (\{c_i, c_j\})$ is the matrix formed from the numbers of intersections of pairs of the curves, and Ω has a self-transformation $\mathcal{T}$ without singular elements on Ω , under which $(\mathcal{T}\mathbf{c}) = \mathbf{T}\mathbf{c}$, then the matrix $\mathbf{T}$ satisfies the equation

$$\mathbf{T}\mathbf{T}\mathbf{T}' = \Gamma.$$

Now let the base $\mathbf{c}$ be replaced by another base $\mathbf{d}$ given by

$$\mathbf{d} = \mathbf{H}\mathbf{c},$$

then

$$\Delta = (\{d_i, d_j\}) = (\{\sum h_{ik}c_k, \sum h_{jl}c_l\}) = \mathbf{H}\Gamma\mathbf{H}', \quad (1.5)$$

and if, referred to this base, the transformation corresponds to the equivalences

$$(\mathcal{T}\mathbf{d}) = \mathbf{U}\mathbf{d},$$

then

$$\mathcal{T}\mathbf{H}\mathbf{c} = \mathbf{H}\mathcal{T}\mathbf{c} = \mathbf{H}\mathbf{T}\mathbf{c} = \mathbf{U}\mathbf{H}\mathbf{c},$$

so that

$$\mathbf{T} = \mathbf{H}^{-1}\mathbf{U}\mathbf{H}. \quad (1.6)$$

As an immediate consequence of equation (1.4) we have

$$1.2 \quad |\mathbf{T}| = \pm 1,$$

but this property of $\mathbf{T}$ is only a part of the following more general property:

1.3. In the characteristic equation of $\mathbf{T}$, namely,

$$|\mathbf{T} - \mathbf{I}x| \equiv x^r + k_1x^{r-1} + \dots + k_r = 0,$$

the coefficients satisfy the conditions

$$(1, k_1, \dots, k_r) = \pm (k_r, \dots, k_1, 1).$$

That is, if ξ is any root of the characteristic equation, so also is ξ^{-1} a root. For

$$\begin{aligned} \Gamma(\mathbf{T}' - \mathbf{I}x)\Gamma^{-1} &= \mathbf{T}\mathbf{T}\mathbf{T}' - \mathbf{I}x \\ &= \mathbf{T}^{-1} - \mathbf{I}x \quad \text{from (1.4)} \\ &= -\mathbf{T}^{-1}(\mathbf{T}x - \mathbf{I}), \end{aligned}$$

so that

$$\begin{aligned} |\mathbf{T} - \mathbf{I}x| &\equiv |\mathbf{T}' - \mathbf{I}x| \equiv |\mathbf{\Gamma}(\mathbf{T}' - \mathbf{I}x)\mathbf{\Gamma}^{-1}| \\ &\equiv |-\mathbf{T}^{-1}| |\mathbf{T}x - \mathbf{I}| \equiv \pm x^r |\mathbf{T} - \mathbf{I}x^{-1}|. \end{aligned}$$

Let $\dots\mathcal{F}^{-1}a, a, \mathcal{F}a, \mathcal{F}^2a, \dots$ be the sequence of curves on Ω determined from a curve a by repeated applications of the transformation $\mathcal{F}$, and let a itself be given by the equivalence

$$a = \alpha'c,$$

α' being a row vector of integers (positive, negative, or zero). Then

$$\begin{aligned} a_1 = \mathcal{F}a &= \mathcal{F}(\alpha'c) = \alpha'Tc, \\ a_2 = \mathcal{F}^2a &= \mathcal{F}^2(\alpha'c) = \alpha'T^2c, \quad \text{etc.} \end{aligned}$$

From the characteristic equation of $\mathbf{T}$,

$$x^r + k_1x^{r-1} + \dots + k_r = 0, \quad (1.7)$$

we derive, for any integral value of s , the matrix identity

$$\mathbf{T}^{s+r} + k_1\mathbf{T}^{s+r-1} + \dots + k_r\mathbf{T}^s = \mathbf{0},$$

and thence the general algebraic equivalence relation

$$\alpha'(\mathbf{T}^{s+r} + k_1\mathbf{T}^{s+r-1} + \dots + k_r\mathbf{T}^s)c = 0$$

connecting the curves $\mathbf{T}^nc$. That is,

1.4. *The curves in any succession of $r+1$ in the sequence $a_n = \mathcal{F}^na$, derived from a curve a by repeated applications of $\mathcal{F}$, are connected by the equivalence relation*

$$a_{r+s} + k_1a_{r+s-1} + \dots + k_ra_s = 0. \quad (1.8)$$

A recurrence relation with these coefficients connects all sequences of numbers associated with the curves (in particular, their orders), but it is not necessarily the simplest such relation (see, for example, equation (9.2)).

Suppose now that $\mathbf{v} = (v_i) = (\{a, c_i\})$,

then $(\mathcal{F}\mathbf{v}) = (\{\mathcal{F}a, c_i\}) = (\{a, \mathcal{F}^{-1}c_i\}) = \mathbf{T}^{-1}\mathbf{v}. \quad (1.9)$

In the problem as usually presented, the transformation $\mathcal{F}$ is defined geometrically, and the matrix $\mathbf{T}$ corresponding to it and associated with some set of base curves, c_i , has to be determined. In these circumstances, as the examples in §§ 8 and 9 will show, it is simpler to calculate the numbers $\mathcal{F}v_i$ from the numbers v_i for a general curve, than it is to calculate $\mathbf{T}$ directly from the transforms of the curves c_i .

The recurrence relation set out in theorem 1.4 has already been discussed in a rather different form (Room (unpublished), part 4, appendix II), and some questions have been raised of its significance, i.e. of the extent to which it characterizes the surface Ω and the self-transformation $\mathcal{F}$. Results obtained in this paper tend towards the conclusion that at best the characterization is very weak. Thus in § 9

we find two birationally distinct quartic surfaces, with distinct self-transformations, both yielding the recurrence relation

$$n_{r+3} - 3n_{r+2} + 3n_{r+1} - n_r = 0. \quad (9.3)$$

Moreover, even $\mathbf{T}$ itself is not characteristic, since in § 8 we find, when the base curves are suitably selected, the same matrix corresponding to the simple self-transformation of a quadric by lines through a point not on it, and to an involutory self-transformation of a quartic surface on which there is a twisted cubic.

On the other hand, for transformations of the same surface it is clear that:

1.5. *If, on a (regular, normal) surface with a given set of base curves, the matrices corresponding to two transformations are identical, then either the transformations themselves are identical, or one is the product of the other with a collineation.*

2. AN ALTERNATIVE APPROACH

In this section we consider first the case of curves on a non-singular quartic surface, and show how the relation (1.4) may be obtained from the equations that express that the genera of curves are invariant under $\mathcal{T}$. We use the following results for (non-singular) curves on a (non-singular) quartic surface.

(i) A curve c of genus p has $2p - 2$ self-intersections, i.e. intersections with another curve of the linear family it defines if $p \geq 1$, and virtual self-intersections if $p = 0$. This is equivalent to

(ii) If c is of genus p , then curves equivalent to $2c$ are of genus $4p - 3$, so that curves equivalent to αc are of genus $\alpha^2(p - 1) + 1$.

Thus if c_1, c_2 of genera p_1, p_2 , have γ_{12} common points, the genus of curves equivalent to $\alpha_1 c_1 + \alpha_2 c_2$ is

$$\pi(\alpha_1 c_1 + \alpha_2 c_2) = \alpha_1^2(p_1 - 1) + \alpha_2^2(p_2 - 1) + \alpha_1 \alpha_2 \gamma_{12} + 1.$$

Write now γ_{ii} for the number of self-intersections of c_i , so that

$$\gamma_{ii} = 2p_i - 2,$$

then
$$\pi(\alpha_1 c_1 + \alpha_2 c_2) = \frac{1}{2}(\gamma_{11}\alpha_1^2 + 2\gamma_{12}\alpha_1\alpha_2 + \gamma_{22}\alpha_2^2) + 1.$$

Now take r curves $c_1, \dots, c_r$ (or $\mathbf{c}$) with intersection-matrix $(\{c_i, c_j\}) = (\gamma_{ij}) = \mathbf{\Gamma}$, the genus of c_i being $\frac{1}{2}\gamma_{ii} + 1$, and an arbitrary row vector, α' , of r integers, then the genus of curves equivalent to $\alpha'c$ is

$$\pi(\alpha'c) = \frac{1}{2}\alpha'\mathbf{\Gamma}\alpha + 1.$$

Finally, let the curves $\mathbf{c}$ form a minimum base on the surface and let them be transformed into curves $\mathcal{T}\mathbf{c}$ equivalent to $\mathbf{Tc}$ under the self-transformation $\mathcal{T}$ of the surface, then

$$\mathcal{T}\alpha'c = \alpha'\mathbf{Tc},$$

$$\pi(\alpha'c) = \frac{1}{2}\alpha'\mathbf{\Gamma}\alpha + 1,$$

$$\pi(\mathcal{T}\alpha'c) = \frac{1}{2}(\alpha'\mathbf{T})\mathbf{\Gamma}(\alpha'\mathbf{T})' + 1$$

$$= \frac{1}{2}\alpha'(\mathbf{T}\mathbf{\Gamma}\mathbf{T}')\alpha + 1.$$

Thus for all values of α' we have

$$\alpha' T \alpha = \alpha' (T T T') \alpha,$$

and thus

2.1. *If a non-singular quartic surface has a self-transformation $\mathcal{T}$, and a minimum base $\mathbf{c}$ such that $(\mathcal{T}\mathbf{c}) = T\mathbf{c}$, and $(\{c_i, c_j\}) = \Gamma$, the condition that expresses that all pairs of corresponding curves $\alpha'\mathbf{c}$, $\mathcal{T}\alpha'\mathbf{c}$ have the same genus is*

$$T T T' = \Gamma.$$

Consider next how this may be applied to a non-singular surface of order n . Statements (i) and (ii) are replaced by (i) a curve c of order m and genus p has $2p - 2 - m(n - 4)$ self-intersections, and (ii) curves equivalent to αc have genus

$$\alpha^2(p - 1) - \frac{1}{2}\alpha(\alpha - 1)m(n - 4) + 1.$$

So that, writing γ_{ii} for the number of self-intersections of c_i , i.e.

$$\gamma_{ii} = 2p_i - 2 - m_i(n - 4),$$

we find that the genus of curves equivalent to $\alpha'\mathbf{c}$ is

$$\pi(\alpha'\mathbf{c}) = \frac{1}{2}\alpha' T \alpha + \frac{1}{2}(n - 4)\alpha' m + 1.$$

If there is a self-transformation $\mathcal{T}$, and $\mathbf{c}$ is a minimum base

$$\pi(\mathcal{T}\alpha'\mathbf{c}) = \pi(\alpha' T \mathbf{c}) = \frac{1}{2}\alpha' T T T' \alpha + \frac{1}{2}(n - 4)\alpha' T m + 1.$$

But

$$\pi(\alpha'\mathbf{c}) = \pi(\mathcal{T}\alpha'\mathbf{c}),$$

and

$$\Gamma = T T T', \quad (1.4)$$

so that

$$\alpha' m = \alpha' T m,$$

i.e. the orders of all curves on the surface remain unchanged under the transformation, thus

2.2. *The only self-transformations of non-singular surfaces of orders greater than four are collineations.*

3. CURVES ON A QUARTIC SURFACE

Let π be a non-singular quartic surface with a minimum base $\mathbf{c}$ containing r curves, of which the intersection matrix is Γ . We wish to find what geometric meaning may be assigned to solutions in integers of the matrix equation

$$X \Gamma X' = \Gamma. \quad (1.4)$$

Two elementary properties may be set down at once:

3.1. *If $\mathbf{X}$ and $\mathbf{Y}$ both satisfy equation (1.4), then their product, $\mathbf{XY}$, also satisfies it.*

In particular, $\mathbf{X}^n$ for all integral values of n , satisfies the equation. Secondly, since $|\mathbf{X}| = \pm 1$ (theorem 1.2), it follows that $\mathbf{X}^{-1}$ is also a matrix of integers, so that

3.2. *If $\mathbf{c}$ is a minimum base, and $\mathbf{X}$ is a solution of (1.4), then $\mathbf{Xc}$ is also a minimum base, all the curves in which have the same genera as the corresponding curves in $\mathbf{c}$.*

Although in general terms it may be said that $\mathbf{X}$ corresponds to a transformation of π into another quartic surface of the same specification (i.e. having on it the same

systems of curves as π), it does not follow that it corresponds to a birational transformation of π into itself. For example, the matrix $\mathbf{X} = \begin{pmatrix} 3, & -1 \\ 1, & 0 \end{pmatrix}$ corresponds to a transformation of one general determinantal quartic surface into another, but not to a transformation of the surface into itself. It happens in this case that $\mathbf{X}^3$ does correspond to a self-transformation of the surface (see § 6 (ii)).

We may draw two negative conclusions:

(i) If (1.4) has no solutions in integers, π can have no self-transformations (other than collineations, since $\mathbf{X} = \mathbf{I}$ always satisfies the equation), nor can there be transformations other than collineations of π into other quartic surfaces.

(ii) If all the curves of $\mathbf{c}$ are proper irreducible curves, and a solution of (1.4) is such that there is no family of proper irreducible curves equivalent to any one of the curves $\mathbf{X}\mathbf{c}$, then there is a no self-transformation of the surface.

Take a particular curve of the set $\mathbf{c}$, say c_1 . If a curve $\Sigma x_{1i}c_i$ has the same genus as it, then

$$\Sigma \gamma_{ij} x_{1i} x_{1j} = \gamma_{11}.$$

This is the first equation of the set (1.4). A solution of this in integers will not necessarily lead to solutions in integers of the whole set (1.4), so that not all curves of the same genus as c_1 are necessarily given by solutions of (1.4).

4. THE BINARY QUADRATIC FORM AND THE PELL EQUATION*

Let
$$\mathbf{\Gamma} = \begin{pmatrix} a & h \\ h & b \end{pmatrix}, \quad (4.1)$$

where $a, b, 2h$ have no common factors,

$$d = h^2 - ab > 0, \quad (4.2)$$

and d is not a square. Also let (ξ, ξ') be the least positive integers other than $(1, 0)$ satisfying the Pell equation

$$x^2 - dx'^2 = 1. \quad (4.3)$$

Then one solution of the matrix equation

$$\mathbf{X}\mathbf{\Gamma}\mathbf{X}' = \mathbf{\Gamma} \quad (1.4)$$

is
$$\mathbf{X}_0 = \begin{pmatrix} \xi - h\xi' & a\xi' \\ -b\xi' & \xi + h\xi' \end{pmatrix}, \quad (4.4)$$

and all other solutions for which $|\mathbf{X}| = +1$ are positive or negative integral powers of $\mathbf{X}_0$, namely,

$$\pm \mathbf{X}_0^n = \pm \frac{1}{2\sqrt{d}} \left[(\xi + \xi'\sqrt{d})^n \begin{pmatrix} \sqrt{d-h} & a \\ -b & \sqrt{d+h} \end{pmatrix} + (\xi - \xi'\sqrt{d})^n \begin{pmatrix} \sqrt{d+h} & -a \\ b & \sqrt{d-h} \end{pmatrix} \right]. \quad (4.5)^\dagger$$

* See, for example, Landau (1927), part I, chapter 7, and part IV, chapter 4. The writer is indebted to Mr W. B. Smith-White of the University of Sydney for pointing out the relation of the present investigation to results for the binary quadratic form, and for suggestions in regard to the Pell equation.

† There are in effect four forms of each solution, corresponding to the selections of sign in $(\pm \xi, \pm \xi')$. All are contained in (4.5). Thus since $(\xi + \xi'\sqrt{d})^{-1} = (\xi - \xi'\sqrt{d})$, $\mathbf{X}_0^{-n}$ is the solution $\mathbf{X}_0^n$ with (ξ, ξ') replaced by $(\xi, -\xi')$.

Moreover, all solutions of $ax^2 + 2hxx' + bx'^2 = a$ (or b) are included in this form.

Now, let U be any solution of (1.4) for which $|U| = -1$, then from the equations leading to theorem 1.3, namely,

$$|U| |U - Ix| = -|Ux - I|,$$

it follows that, for matrices of order 2,

$$U^2 = I. \quad (4.6)$$

If U, V , with $|U| = -1, |V| = -1$, are two solutions of (1.4), then UV is a solution with $|UV| = +1$, and thus for some value of r

$$UV = \pm X'_0,$$

so that all solutions with negative determinant are of the form $\pm UX'_0$, where U is any one such solution.

Next suppose that Γ is such that the highest common factor of $a, b, 2h$ is 2, that

$$d = h^2 - ab > 0,$$

and is not a square, and that (η, η') is the least solution in positive integers, other than $(2, 0)$, of the modified Pell equation

$$y^2 - dy'^2 = 4. \quad (4.7)$$

then

$$Y_0 = \frac{1}{2} \begin{pmatrix} \eta - h\eta' & a\eta' \\ -b\eta' & \eta + h\eta' \end{pmatrix} \quad (4.8)$$

is a solution of (1.4), and all other solutions with positive determinant are of the form $\pm Y_0^n$, and those with negative determinant are formed as before.

If $a, b, 2h$ have common factors other than 2, these factors must first be removed, and the resulting equation (1.4) treated in one of the two ways set out above.

If $d = h^2 - ab$ is a square, there are no solutions other than $X = I$ with positive determinant, and, in consequence, at most one solution with negative determinant.

5. QUARTIC SURFACES WITH A MINIMUM BASE CONTAINING TWO CURVES

Let a quartic surface π be specialized only by being made to contain a non-singular curve of order m and genus p ; we wish to find what families of curves lie on π in consequence of this, and what self-transformations, if any, π has. Take as base curves on π :

c_1 : a plane section,

c_2 : the curve of order m and genus p .*

The intersection matrix is
$$\Gamma = \begin{pmatrix} 4 & m \\ m & 2q \end{pmatrix}, \quad (5.1)$$

where

$$q = p - 1.$$

* The assumption is made here, and in all corresponding places, that no further curves are necessary to constitute the base.

We find first a solution $\mathbf{U}$ of the equation

$$\mathbf{X}\mathbf{F}\mathbf{X}' = \mathbf{\Gamma} \quad (1.4)$$

for which $|\mathbf{U}| = -1$. Rewrite (1.4) in the form

$$\mathbf{U}^{-1}\mathbf{\Gamma} = \mathbf{\Gamma}\mathbf{U}', \quad (5.2)$$

and let

$$\mathbf{U} = \begin{pmatrix} u & v \\ u' & v' \end{pmatrix},$$

where

$$uv' - u'v = -1.$$

Then, from (5.2),

$$u' = \frac{1}{2}(mu + qv), \quad v' = -u, \quad (5.3)$$

and from the first equation of the set (1.4), namely,

$$4u^2 + 2mu v + 2qv^2 = 4,$$

we find

$$u = \frac{1}{4}\{-mv \pm \sqrt{(kv^2 + 16)}\}, \quad (5.4)$$

where

$$k = m^2 - 8q.$$

A solution of (1.4) is

$$\mathbf{U} = \begin{pmatrix} \frac{1}{4}(w - mv) & v \\ \frac{1}{8}\{mw - (k + 4q)v\} & -\frac{1}{4}(w - mv) \end{pmatrix}, \quad (5.5)$$

where (v, w) is a solution of the modified Pell equation

$$w^2 - kv^2 = 16. \quad (5.6)$$

The solution has to be selected in such a way that all the terms in $\mathbf{U}$ are integers. If m is even

$$\mathbf{W} = \begin{pmatrix} 1 & 0 \\ \frac{1}{2}m & -1 \end{pmatrix} \quad (5.7)$$

is a solution for all values of q .

The solutions of (1.4) with positive determinant can all be reduced to the forms given in equations (4.4), (4.5), (4.8), with

$$a = 4, \quad h = m, \quad b = 2q, \quad d = m^2 - 8q = k.$$

We have first to verify that k is positive. This is a special case of a theorem due to Hodge (1937), namely, 'there is exactly one positive term in the signature of the intersection matrix of a base for the algebraic curves on a surface.' More simply, we may in this case use the theorem: 'the curve of maximum genus for a given order on a non-singular surface is either a complete section, or residual to a partial plane section.' For a quartic surface and curves of order m we have

$$\begin{array}{lll} m = 4r, & p_{\max.} = 2r^2 + 1, & m^2 - 8(p_{\max.} - 1) = 0, \\ & 4r \pm 1, & 2r^2 \pm r, & 9, \\ & 4r + 2, & 2r^2 + 2r, & 12. \end{array}$$

Thus:

5.1. *If an irreducible non-singular curve of order m on a quartic surface has genus $q + 1$, and is not a complete section then*

$$k = m^2 - 8q = 8r, \quad \text{or} \quad 8r + 1, \quad \text{or} \quad 8r + 4, \quad \text{where} \quad r \geq 1.$$

Consider first the cases in which

$$8 < k = m^2 - 8q = \text{a square} = h^2, \text{ say,}$$

i.e. those for which the only solution with positive determinant is the trivial $\mathbf{X} = \mathbf{I}$. For other solutions we have, from (5.6),

$$w^2 - (hv)^2 = 16.$$

If $h^2 \neq 9$, the only pair of values is $v = 0, w = 4$, giving the matrix $\mathbf{W}$ (equation (5.7)) for even values of m , and no solution for odd values of m .

If $h^2 = 9$ we have in addition $v = 1, w = 5$, and if $m = 4s + 1$,

$$\mathbf{U} = \begin{pmatrix} s-1 & -1 \\ s(s-2) & -(s-1) \end{pmatrix}$$

is a proper algebraic solution. But the curve given by these values of m and q is residual to a plane cubic, and the surface therefore contains a line, which may be taken to be the specialization instead of the curve c_2 (see § 7 (i)), so that this case does not require separate consideration.

Thus there are only two cases for which

$$k = h^2,$$

- (i) m odd, no non-trivial solution,
- (ii) m even, one solution, namely, $\mathbf{W}$.

Consider next the solutions for values of k which are not squares. We have to take account of common factors among 4, $2m$, $2q$, and find four distinct cases:

$$(iii) \quad m = 2r + 1 \quad \mathbf{Y} = \frac{1}{2} \begin{pmatrix} \eta - m\eta' & 4\eta' \\ -2q\eta' & \eta + m\eta' \end{pmatrix}, \quad \eta^2 - k\eta'^2 = 4.$$

$$(iv) \quad \left. \begin{matrix} m = 2r \\ q = 2s + 1 \end{matrix} \right\} \quad \mathbf{X} = \begin{pmatrix} \xi - \frac{1}{2}m\xi' & 2\xi' \\ -q\xi' & \xi + \frac{1}{2}m\xi' \end{pmatrix}, \quad \xi^2 - \frac{1}{4}k\xi'^2 = 1.$$

$$(v) \quad \left. \begin{matrix} m = 4r + 2 \\ q = 2s \end{matrix} \right\} \quad \mathbf{Y} = \frac{1}{2} \begin{pmatrix} \eta - \frac{1}{2}m\eta' & 2\eta' \\ -q\eta' & \eta + \frac{1}{2}m\eta' \end{pmatrix}, \quad \eta^2 - \frac{1}{4}k\eta'^2 = 4.$$

$$(vi) \quad \left. \begin{matrix} m = 4r \\ q = 2s \end{matrix} \right\} \quad \mathbf{X} = \begin{pmatrix} \xi - \frac{1}{4}m\xi' & \xi' \\ -\frac{1}{2}q\xi' & \xi + \frac{1}{4}m\xi' \end{pmatrix}, \quad \xi^2 - \frac{1}{16}k\xi'^2 = 1.$$

6. SOME SPECIAL QUARTIC SURFACES WITH TWO BASE CURVES

(i) The surfaces for which $k = h^2$

The geometric result corresponding to the two cases (i), (ii) of § 5 is

6.1. *If a quartic surface is specialized only in such a way as to make it contain a non-singular curve c of order m and genus $q + 1$, and $m^2 - 8q$ is a square, then, if m is odd, there are no curves of the same genus as c on the surface other than those belonging*

to the linear family defined by c , and, if m is even, none beside that linear family, and the family of curves of the same order residual to it.

If the quartic surface is made to contain a non-singular elliptic curve of order m , then $q = 0$, and the conditions above apply, i.e.

7.2. *If a quartic surface is specialized only in such a way as to make it contain a non-singular elliptic curve, e , of order m , then the only elliptic curves on the surface are, if m is odd, the pencil determined by e , and, if m is even, that pencil and the pencil of curves of the same order residual to it.*

(ii) *The determinantal quartic surface*

If a quartic surface contains a Schur sextic curve of genus three, then it contains two residual ∞^3 families of such curves and is representable by the vanishing of a determinant of linear forms. Take as base a plane section c_1 , and a Schur sextic, c_2 . Then $m = 6$, $2q = 4$, $k = 20$, and the surface is of type (v) of § 5. The solutions of the equation (1.4) that have positive determinant are

$$\mathbf{Y} = \frac{1}{2} \begin{pmatrix} \eta - 3\eta' & 2\eta' \\ -2\eta' & \eta + 3\eta' \end{pmatrix},$$

where (η, η') is a solution of $\eta^2 - 5\eta'^2 = 4$.

The smallest significant solution in positive integers is (3, 1), leading to

$$\mathbf{Y}_0 = \begin{pmatrix} 0 & 1 \\ -1 & 3 \end{pmatrix}, \quad \mathbf{Y}_0^{-1} = \begin{pmatrix} 3 & -1 \\ 1 & 0 \end{pmatrix}.$$

These matrices do not correspond to self-transformations, but

$$\mathbf{Y}_0^{-3} = \begin{pmatrix} 21 & -8 \\ 8 & -3 \end{pmatrix}$$

corresponds to the well-known self-transformation of the determinantal quartic surface, which is represented, roughly, by the interchange of the parts played by the rows and columns in the determinant.*

The principal solution with negative determinant is

$$\mathbf{V} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

The principal geometric solution is

$$\mathbf{Y}_0 \mathbf{V} = \begin{pmatrix} 1 & 0 \\ 3 & -1 \end{pmatrix},$$

which corresponds to an interchange of the parts played by the two systems of Schur sextics.

* Due originally to Schur (1882), p. 256. See also Jessop (1916, p. 163), and Room (unpublished, parts 1 to 5).

7. QUARTIC SURFACES WITH TWO BASE CURVES, ONE OF THEM RATIONAL

Let a quartic surface π be specialized only by being made to contain a non-singular rational curve of order m ; we wish to determine what other rational curves lie on the surface in consequence.*

Take as base curves on the surface

c_1 : a plane section,

c_2 : the rational curve of order m ,

$$\mathbf{\Gamma} = \begin{pmatrix} 4 & m \\ m & -2 \end{pmatrix}, \quad k = m^2 + 8.$$

A rational curve on a quartic surface does not define a linear system of curves, so that if $c = n_1 c_1 + n_2 c_2$ is a rational curve, and $n_1 > 0$, $n_2 > 0$, the only curve equivalent to c is c itself, namely the reducible curve consisting of the section of π by a surface of order n_1 together with c_2 counted n_2 times. Again, if n_1 is negative and equal to $-n'_1$, the equation $c + n'_1 c_1 = n_2 c_2$ is devoid of geometrical significance, but if

$$n_1 > 0, \quad n_2 = -n'_2 < 0,$$

the curve may be proper, namely the residual curve cut out by a surface of order n_1 which cuts π in c_2 counted n'_2 times.

Rational curves on the surface are given by solutions of the equation

$$4n_1^2 + 2mn_1 n_2 - 2n_2^2 = -2,$$

but the only solutions which can lead to proper curves are those for which

$$n_1 > 0, \quad n_2 < 0.$$

All solutions of this equation are included in the solutions of the matrix equation

$$\mathbf{X}\mathbf{\Gamma}\mathbf{X}' = \mathbf{\Gamma}. \quad (1.4)$$

We need only one basic solution with negative determinant; this may be taken to be

$$\mathbf{U} = \begin{pmatrix} 1 & m \\ 0 & -1 \end{pmatrix}. \quad (7.1)$$

For even values of m we have another such solution, namely,

$$\mathbf{W} = \begin{pmatrix} 1 & 0 \\ \frac{1}{2}m & -1 \end{pmatrix}, \quad (5.7)$$

$$\text{so that} \quad \mathbf{X}_0 = \mathbf{W}\mathbf{U} = \begin{pmatrix} 1 & m \\ \frac{1}{2}m & \frac{1}{2}m^2 + 1 \end{pmatrix} \quad (7.2)$$

is one solution with positive determinant.

* The freedom of rational curves of order m is $4m$, and the number of conditions imposed on a quartic surface in making it contain the curve is $4m + 1$. Thus the freedom of quartic surfaces which contain an unspecified rational curve is one less than the freedom of general surfaces, namely, 33. Likewise the freedom of quartic surfaces containing any unspecified curve of order m and genus p is 33 (provided $p \neq \frac{1}{2}m^2 + 1$), but such a surface contains a linear family of freedom p of such curves.

For general solutions with positive determinant we have:

$$m \text{ odd: } \mathbf{Y} = \frac{1}{2} \begin{pmatrix} \beta' - m\beta & 4\beta \\ 2\beta & \beta' + m\beta \end{pmatrix} \quad (7.3)$$

$$\text{for any } (\beta, \beta') \text{ which satisfies } \beta'^2 - (m^2 + 8)\beta^2 = 4, \quad (7.4)$$

$$m \text{ even: } \mathbf{X} = \begin{pmatrix} \alpha' - \frac{1}{2}m\alpha & 2\alpha \\ \alpha & \alpha' + \frac{1}{2}m\alpha \end{pmatrix}, \quad (7.5)$$

$$\text{for any } (\alpha, \alpha') \text{ which satisfies } \alpha'^2 - \frac{1}{4}(m^2 + 8)\alpha^2 = 1. \quad (7.6)$$

Now consider in more detail the solution for odd values of m . Suppose β, β' are both positive and are *any* solution of (7.4). Then all the elements in $\mathbf{Y}$ are positive, and the various possible arrangements of sign are

$$\mathbf{Y} = \begin{pmatrix} + & + \\ + & + \end{pmatrix}, \quad \mathbf{Y}^{-1} = \begin{pmatrix} + & - \\ - & + \end{pmatrix}, \quad -\mathbf{Y} = \begin{pmatrix} - & - \\ - & - \end{pmatrix}, \quad -\mathbf{Y}^{-1} = \begin{pmatrix} - & + \\ + & - \end{pmatrix}.$$

Of these only the last can yield a proper rational curve. Next:

$$\begin{aligned} \mathbf{UY} &= \frac{1}{2} \begin{pmatrix} \beta' + m\beta & m\beta' + (m^2 + 4)\beta \\ -2\beta & -(\beta' + m\beta) \end{pmatrix}, \\ \mathbf{YU} = \mathbf{UY}^{-1} &= \frac{1}{2} \begin{pmatrix} \beta' - m\beta & m\beta' - (m^2 + 4)\beta \\ 2\beta & -(\beta' - m\beta) \end{pmatrix}. \end{aligned}$$

From (7.4) it follows that $\beta' - m\beta > 0$ and $m\beta' - (m^2 + 4)\beta < 0$ if $\beta > \frac{1}{2}m$, so that of the four matrices $+\mathbf{UY}$, $-\mathbf{UY}$, $-\mathbf{UY}^{-1}$, $+\mathbf{UY}^{-1}$, only the last can yield a proper rational curve, namely, the same curve as is given by $-\mathbf{Y}^{-1}$. But $\mathbf{UY}^{-1}$ has the advantage that it may also give a proper curve to replace the plane section. Thus if the surface has a self-transformation the corresponding matrix must be one of the matrices $\mathbf{UY}^{-1}$. There are corresponding results for the matrices $\mathbf{X}$ and $\mathbf{U}$ for even values of m . Thus

7.1. *If a quartic surface is specialized only by being made to contain a rational curve, then it has at most one self-transformation, and that transformation is involutory.*

We conclude this section by discussing briefly the surfaces with rational curves of orders $m = 0, 1, 2$, and in § 8 we discuss more fully the surface on which there is a twisted cubic.

(i) $m = 0$. *The surface with an ordinary node*

$$\begin{aligned} \mathbf{\Gamma} &= \begin{pmatrix} 4 & 0 \\ 0 & -2 \end{pmatrix}, \quad \mathbf{U} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \mathbf{Y}_0 = \begin{pmatrix} 3 & 4 \\ 2 & 3 \end{pmatrix}, \\ \mathbf{Y}_0 \mathbf{U} &= \mathbf{UY}_0^{-1} = \begin{pmatrix} 3 & -4 \\ 2 & -3 \end{pmatrix}. \end{aligned}$$

The rational curve derived from $\mathbf{Y}_0 \mathbf{U}$, namely, $2c_1 - 3c_2$, an octavic with a 6-ple point at the node, is a proper curve. It is the intersection of π with the tangent cone at the node. $\mathbf{Y}_0 \mathbf{U}$, in fact, corresponds to the involution determined on the surface by lines through the node. Next

$$\mathbf{Y}_0^2 \mathbf{U} = \begin{pmatrix} 17 & -24 \\ 12 & -17 \end{pmatrix}.$$

Since $12c_1 - 18c_2 = 6(2c_1 - 3c_2)$, it seems not improbable that the curve $12c_1 - 17c_2$ is a proper curve, and likewise that the rational curve obtained from all matrices Y_0U , for positive powers, are proper.

(ii) $m = 1$. *The surface with a line*

$$\Gamma = \begin{pmatrix} 4 & 1 \\ 1 & -2 \end{pmatrix}, \quad k = 9, \quad U = \begin{pmatrix} 1 & 1 \\ 0 & -1 \end{pmatrix}.$$

Equation (7.4) becomes $\beta'^2 - 9\beta^2 = 4$,

of which the only solution is $\beta' = \pm 2$, $\beta = 0$, giving $Y = \pm I$, and $\pm U$. Thus

7.2. *A quartic surface specialized only by being made to contain a line contains no other rational curves.*

(iii) $m = 2$. *The surface with two coplanar conics*

Take the two conics as base curves, so that

$$\Gamma = \begin{pmatrix} -2 & 4 \\ 4 & -2 \end{pmatrix},$$

and solutions are derived as in § 5 (v). The Pell equation is

$$x'^2 - 3x^2 = 1,$$

leading to $X_0 = \begin{pmatrix} 0 & -1 \\ 1 & 4 \end{pmatrix}$, $X_0^{-1} = \begin{pmatrix} 4 & 1 \\ -1 & 0 \end{pmatrix}$, $V = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$.

In any matrix X_0^n , or VX_0^n the elements of one row are both positive and the elements of the other both negative, thus

7.3. *A quartic surface specialized only so that it contains two coplanar conics has on it no other proper rational curves.*

8. THE QUARTIC SURFACE WITH A TWISTED CUBIC

Let π be a quartic surface specialized only by being made to pass through a twisted cubic. Take as base curves on π

- c_1 : a plane section,
- c_2 : the twisted cubic.

Then

$$\Gamma = \begin{pmatrix} 4 & 3 \\ 3 & -2 \end{pmatrix},$$

and the algebraic solution of equation (1.4) with positive determinant is

$$Y = \frac{1}{2} \begin{pmatrix} \eta - 3\eta' & 4\eta' \\ 2\eta' & \eta - 3\eta' \end{pmatrix},$$

where

$$\eta^2 - 17\eta'^2 = 4.$$

The least positive integers satisfying this equation are (66, 16) so that

$$Y_0 = \begin{pmatrix} 9 & 32 \\ 16 & 57 \end{pmatrix}.$$

An algebraic solution with negative determinant is

$$U = \begin{pmatrix} 1 & 3 \\ 0 & -1 \end{pmatrix},$$

and the two simplest solutions which may be capable of geometric interpretation are

$$Y_0 U = \begin{pmatrix} 9 & -5 \\ 16 & -9 \end{pmatrix}$$

and

$$Y_0^2 U = \begin{pmatrix} 593 & -333 \\ 1056 & -593 \end{pmatrix}.$$

$Y_0 U$ corresponds, as we see immediately, to a self-transformation of the surface, and so yields proper curves, of which the rational curve is given as $16c_1 - 9c_2$. But $1056c_1 - 593c_2 = 66(16c_1 - 9c_2) + c_2$, so that there is no proper rational curve determined by $Y_0^2 U$. Likewise every matrix $Y_0^n U$ yields a curve $\lambda(16c_1 - 9c_2) + \mu c_2$ with λ, μ positive, and there are therefore no other rational curves on the surface.

Let us consider now the geometric determination of the self-transformation of the surface. Through any point of π a single chord of c_2 may be drawn, and this chord meets π in one further point, so that chords of c_2 establish an involution $\mathcal{P}$ on π . To construct the matrix $\mathbf{P}$ corresponding to $\mathcal{P}$ we have to determine from the numbers $n_i = \{a, c_i\}$ for a general curve, a , the numbers $\mathcal{P}n_i = \{\mathcal{P}a, c_i\}$ (cf. equation (1.9)).

By degeneration methods we find that the chords of c_2 which meet a form a surface of order $4n_1 - 2n_2$ on which c_2 is $(2n_1 - n_2)$ -ple. Thus $\mathcal{P}n_1$, which is the order of the residual intersection of this surface with π , is given by

$$\mathcal{P}n_1 = 4(4n_1 - 2n_2) - 3(2n_1 - n_2) - n_1 = 9n_1 - 5n_2.$$

Since the transformation is involutory

$$\mathcal{P}^{-1}c_1 = \mathcal{P}c_1 = 9c_1 - 5c_2,$$

and we may complete the matrix $\mathbf{P}$ from equation (1.4), or from $\mathbf{P}^2 = \mathbf{I}$. We find

$$\mathbf{P} = \begin{pmatrix} 9 & -5 \\ 16 & -9 \end{pmatrix}.$$

$\mathcal{P}c_2$ is the curve cut out by chords of c_2 which are tangents to π at one of their intersections with π . One tangent of π at a point of c_2 meets c_2 again, and seven chords of c_2 through a point of c_2 touch π at their second intersection with c_2 . Thus on the surface of chords of c_2 tangent to π at one of their intersections with c_2 , the curve c_2 is altogether 8-ple, but one of the sheets of the surface touches π all along c_2 , so that its total intersection with π is c_2 counted 9 times, together with $\mathcal{P}c_2$. This is in conformity with the figures in the matrix which set out that $\mathcal{P}c_2 + 9c_2$ is the complete section of π by a surface of order 16.

To determine the order of the double curve, p , of the involution, we may allow c_2 to degenerate into two skew lines l, l' , and a transversal m . Transversals of l, l' which are tangent to π elsewhere form a surface of order 8 on which l, l' are 4-ple. The line m is double on this surface, so that the residual intersection of the surface with π is a curve of order 11, counted twice. The lines which meet l and m and are tangent elsewhere touch the residual conic in the plane of l and m . Thus the order of the complete double curve is 15, and therefore in the case of a non-degenerate cubic c_2 , the chords of c_2 which are tangent elsewhere form a surface of order 12 on which c_2 is 6-ple, and which cuts π residually in p counted twice, i.e.

$$2p = 12c_1 - 6c_2.$$

The genus of $12c_1 - 6c_2$ is 37, so that the genus of p is 10.

This surface and transformation provide an illustration of how little even the matrix corresponding (for a certain base) to the transformation is characteristic. Consider the simple involution $\mathcal{D}$ of a quadric Δ determined by lines through a point not on Δ . The effect of $\mathcal{D}$ is to interchange the generators of the two systems, so that if the base curves $\mathbf{g} = (g_1, g_2)$ on Δ are taken to be one generator of each system, we have

$$\mathcal{D}\mathbf{g} = \mathbf{D}\mathbf{g},$$

where

$$\mathbf{D} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

But the matrix

$$\mathbf{K} = \begin{pmatrix} 2 & 3 \\ 3 & 5 \end{pmatrix}$$

is such that

$$\mathbf{K}\mathbf{D}\mathbf{K}^{-1} = \mathbf{P},$$

so that

$$\mathcal{D}(\mathbf{K}\mathbf{g}) = \mathbf{K}(\mathcal{D}\mathbf{g}) = \mathbf{K}\mathbf{D}\mathbf{g} = \mathbf{P}\mathbf{K}\mathbf{g}.$$

Explicitly

$$\mathcal{D}\begin{pmatrix} 2g_1 + 3g_2 \\ 3g_1 + 5g_2 \end{pmatrix} = \begin{pmatrix} 9 & -5 \\ 16 & -9 \end{pmatrix} \begin{pmatrix} 2g_1 + 3g_2 \\ 3g_1 + 5g_2 \end{pmatrix}.$$

Thus the matrix corresponding to the transformation $\mathcal{D}$ of Δ , when we take as base curves on Δ :

$$\text{a } (3, 2)\text{-curve, } g'_1 = 2g_1 + 3g_2,$$

and

$$\text{a } (5, 3)\text{-curve, } g'_2 = 3g_1 + 5g_2,$$

is identical with the matrix $\mathbf{P}$ of the self-transformation $\mathcal{P}$ of π . The intersection matrix of Δ is

$$(\{g'_i, g'_j\}) = \begin{pmatrix} 12 & 19 \\ 19 & 30 \end{pmatrix}.$$

The double curve d of $\mathcal{D}$ is a certain plane section, i.e.

$$\begin{aligned} 2d &= 2(g_1 + g_2) = 2\{(5g'_1 - 3g'_2) + (-3g'_1 + 2g'_2)\} \\ &= 4g'_1 + 2g'_2. \end{aligned}$$

The essential feature of the matrix $\mathbf{K}$ defined so that $\mathbf{KDK}^{-1} = \mathbf{P}$ is that both $\mathbf{K}$ and $\mathbf{K}^{-1}$ are composed of integers. Thus the curves g'_i on Δ are proper curves, and the generators (curves g_i) may be cut out (one at a time) by surfaces determined by these curves.*

An example of a self-transformation of a quartic surface with two base curves which cannot be made to correspond to the transformation $\mathcal{Q}$ is provided by the quartic surface with an ordinary node N , which was discussed in § 7 (i). The matrix corresponding to the involution determined by lines through N is

$$\mathbf{N} = \begin{pmatrix} 3 & -4 \\ 2 & -3 \end{pmatrix}.$$

Let

$$\mathbf{H} = \begin{pmatrix} p & q \\ r & s \end{pmatrix},$$

with

$$ps - qr = \epsilon = \pm 1,$$

be such that

$$\mathbf{H}\mathbf{D}\mathbf{H}^{-1} = \mathbf{N}.$$

Then

$$2p = 3r + s, \quad 2q = r + 3s, \quad ps - qr = \epsilon,$$

i.e.

$$s^2 - r^2 = 2\epsilon.$$

This equation has no solution in integers, so that no matrix $\mathbf{H}$ of the type required exists.

9. A TERNARY QUADRATIC FORM, AND INVOLUTIONS ON CERTAIN QUARTIC SURFACES

A general attack on the problem of solving the set of diophantine equations

$$\mathbf{X}\mathbf{F}\mathbf{X}' = \mathbf{T} \tag{1.4}$$

for matrices of order 3, is not at present contemplated, but some indication of the possible solutions in certain cases may be obtained by constructing quartic surfaces with three base curves which have geometrically definable self-transformations.

One such family of quartic surfaces may be established by making use of the following theorem:

9.1. *If two curves are such that through any point of space one and only one line can be drawn to meet the curves in distinct points, then one of the curves is a straight line, and the other is a rational curve of order m to which the line is $(m-1)$ -secant.*

Thus the most general involutory transformation of a quartic surface that may be determined by 'chords' of some reducible curve on the surface, is that of a surface

* A surface of order 10 through two curves g'_i cuts out four generators g_i on Δ ; a surface of order 10 through these four generators and three curves g'_i , cuts Δ residually in a single generator g_s .

that contains a rational curve of order m and an $(m-1)$ -secant line of the curve. Let π be such a surface, with a self-transformation $\mathcal{R}$, and on it take as base:

- c_1 : a plane section,
- c_2 : the line,
- c_3 : the rational curve of order m to which c_2 is $(m-1)$ -secant,

$$\mathbf{I} = \begin{pmatrix} 4 & 1 & m \\ 1 & -2 & m-1 \\ m & m-1 & -2 \end{pmatrix}.$$

To any self-transformation of the surface corresponds a solution of the six diophantine equations

$$4x_ix_j - 2y_iz_j - 2z_iz_j + (m-1)(y_iz_j + y_jz_i) + m(z_ix_j + z_jx_i) + (x_iy_j + x_jy_i) = \gamma_{ij}. \quad (9.1)$$

For a given curve a let $\nu_i = \{a, c_i\}$,

then, by allowing a to degenerate into an appropriate set of ν_1 lines, we find that the order $\mathcal{R}\nu_1$ of $\mathcal{R}a$ is* $\mathcal{R}\nu_1 = (2m+3)\nu_1 - (2m+1)\nu_2 - 3\nu_3$.

From this, and (1.4), and $\mathbf{R}^2 = \mathbf{I}$ it follows that

$$\mathbf{R} = \begin{pmatrix} 2m+2 & -2m-1 & -3 \\ 2m+2 & -2m-1 & -3 \\ 2m+2 & -2m-1 & -3 \end{pmatrix} + \mathbf{I}.$$

The recurrence relation derived from the characteristic equation of $\mathbf{R}$ is

$$n_{r+3} - n_{r+2} - n_{r+1} + n_r = 0 \quad (9.2)$$

(whereas the 'true' recurrence relation is of course $n_{r+2} - n_r = 0$).

Next $\{\{\mathcal{R}c_i, c_j\}\} = \mathbf{R}\mathbf{I} = \begin{pmatrix} 3m+11 & 3m+8 & 4m+7 \\ 3m+8 & 3m+5 & 4m+6 \\ 4m+7 & 4m+6 & 3m+5 \end{pmatrix}.$

The important figures are

$$\{\mathcal{R}c_3, c_1\} = 4m+7, \quad \{\mathcal{R}c_3, c_2\} = 4m+6.$$

Thus

9.2. The curve $\mathcal{R}c_3$ is a rational $(4m+7)$ -ic to which the line c_2 is $(4m+6)$ -secant, and the surface consequently has a second self-transformation $\mathcal{R}_1$, determined by $\mathcal{R}c_3$ and c_2 , and thence a sequence of self-transformations each determined by c_2 and the transform of the fundamental curve in the preceding member of the sequence.

Replacing m by $4m+7$ in the matrix $\mathbf{R}$ we find

$$\mathcal{R}_1 \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 8m+17 & -8m-15 & -3 \\ 8m+16 & -8m-14 & -3 \\ 8m+16 & -8m-15 & -2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}.$$

* Suppose that $\nu_1 \geq \nu_2 + \nu_3$; then let a consist of $\nu_1 - \nu_2 - \nu_3$ lines l_1 not meeting c_2 or c_3 , ν_2 lines l_2 meeting c_2 only, and ν_3 lines l_3 meeting c_3 only. Let μ_i be the order of the residual curve cut out by lines which meet a line l_i and c_2 and c_3 , then it may easily be proved that $\mu_1 = 2m+3$, $\mu_2 = 2$, $\mu_3 = 2m$, so that the order of the residual curve cut out by lines meeting a , c_2 , c_3 is $(2m+3)(\nu_1 - \nu_2 - \nu_3) + 2\nu_2 + 2m\nu_3$. The case $\nu_1 < \nu_2 + \nu_3$ may be dealt with similarly by allowing some of the lines to meet both c_2 and c_3 .

But

$$\mathcal{R}c_3 = (2m+2)c_1 - (2m+1)c_2 - 2c_3,$$

so that

$$\mathcal{R}_1 \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2m+11 & -2m-12 & 6 \\ 2m+10 & -2m-11 & 6 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}.$$

The result $\mathcal{R}_1 c_3 = c_3$ is to be expected, since $\mathcal{R}c_3$ is the curve cut out by tangents to π along c_3 that meet c_2 . Thus, in $\mathcal{R}_1$, c_3 is part of the curve cut out by the lines which meet c_2 and $\mathcal{R}c_3$, and touch π elsewhere. In effect, c_3 is part of the double curve of $\mathcal{R}_1$.

The curve $\mathcal{R}_1 \mathcal{R}c_3$ is of order $4(4m+7)+7 = 16m+35$, and to it c_2 is $(16m+34)$ -secant. For the involution $\mathcal{R}_2$ determined by these we find

$$\mathcal{R}_2 \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 20m+37 & -20m-32 & -12 \\ 20m+36 & -20m-31 & -12 \\ 10m+18 & -10m-16 & -5 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}.$$

For the matrices corresponding to $\mathcal{R}$, $\mathcal{R}_1$, $\mathcal{R}_2$, we find

$$\mathbf{R}_1 \mathbf{R} = \mathbf{R} \mathbf{R}_2 = \begin{pmatrix} 12m+21 & -12m-17 & -9 \\ 12m+20 & -12m-16 & -9 \\ 2m+2 & -2m-1 & -2 \end{pmatrix} = \mathbf{S}, \text{ say,}$$

so that

$$\mathcal{R}_2 = \mathcal{R} \mathcal{R}_1 \mathcal{R}.$$

This relation is true of any three successive transformations in the sequence, thus

9.3. *If $\mathcal{R}_i$ is a transformation of the sequence defined in theorem 9.2, then*

$$\mathcal{R}_{i+2} = \mathcal{R}_i \mathcal{R}_{i+1} \mathcal{R}_i,$$

and all transformations of the sequence may be expressed as products of $\mathcal{R}$ with powers of $\mathcal{S} = \mathcal{R}_1 \mathcal{R}$.

We have, in fact, two sequences of transformations of π :

$$\mathcal{S}^n (= \mathcal{R} \mathcal{S}^{-n} \mathcal{R}) \quad \text{which are not involutory,}$$

and

$$\mathcal{R} \mathcal{S}^n (= \mathcal{S}^{-n} \mathcal{R}) \quad \text{which are involutory.}$$

From the characteristic equation of $\mathbf{S}$ we find the recurrence relation for numbers associated with a sequence of curves

$$\dots \mathcal{S}^{-1}a, \quad a, \quad \mathcal{S}a, \quad \mathcal{S}^2a, \quad \dots$$

to be*

$$n_{r+3} - 3n_{r+2} + 3n_{r+1} - n_r = 0, \quad (9.3)$$

* This is the same as the recurrence relation for one of the sequences of transformations of a quartic surface on which there is a twisted cubic and a non-incident line. This surface (see, for example, Room (unpublished) parts 2, 4 appendix II, and 5) is determinantal and has two distinct sequences of self-transformations, derived from $\mathcal{S}$, the Schur self-transformation, and $\mathcal{U}$, the involution determined by chords of the cubic. With a plane section, the line, and the twisted cubic as base curves we find

$$\mathbf{T} = \begin{pmatrix} 4 & 1 & 3 \\ 1 & -2 & 0 \\ 3 & 0 & -2 \end{pmatrix}, \quad \mathbf{T} = \begin{pmatrix} 13 & 5 & -8 \\ 8 & 4 & -5 \\ 0 & 1 & 0 \end{pmatrix}, \quad \mathbf{U} = \begin{pmatrix} 9 & 0 & -5 \\ 4 & -1 & -2 \\ 16 & 0 & -9 \end{pmatrix} \quad \text{and} \quad \mathbf{TU} = \begin{pmatrix} 9 & -5 & -3 \\ 8 & -4 & -3 \\ 4 & -1 & -2 \end{pmatrix}.$$

The recurrence relation for $\mathbf{TU}$ is (9.3).

and in consequence

$$n_r = A + Br + Cr^2,$$

where the values of A, B, C are determined by the particular sequence under consideration. The elements of the powers of $\mathbf{S}$ form such sequences, and we find in this way that

$$\mathbf{S}^r = r^2 \begin{pmatrix} 9m+21 & -9m-21 & 0 \\ 9m+21 & -9m-21 & 0 \\ 3m+7 & -3m-7 & 0 \end{pmatrix} + r \begin{pmatrix} 3m-1 & -3m+4 & -9 \\ 3m-1 & -3m+4 & -9 \\ -m-5 & m+6 & -3 \end{pmatrix} + \mathbf{I}.$$

These and the matrices $\mathbf{RS}^r$ provide some of the solutions to the diophantine equations (9.1).

The transformations $\mathcal{S}^n$ and $\mathcal{RS}^n$ are not necessarily all the self-transformations of the surface as the following examples show:

$m = 1$. There are two separate sequences of transformations (and all their products) obtained by making each of the lines in turn play the part of c_3 .

$m = 3$. There is a further involutory transformation determined from chords of the twisted cubic c_3 as in § 8.

$m = 4$. The curve c_3 is a rational quartic and c_2 is a trisecant of it so that $c_2 + c_3$ lies on a quadric. Thus $2c_1 - c_2 - c_3$ is a twisted cubic and determines a further involution as in § 8.

$m = 5$. The curve c_3 is a rational quintic, and c_2 is its single quadrisecant line; $c_2 + c_3$ is a sextic of genus three, and the quartic surface is thus determinantal, and has the sequence of self-transformations corresponding to those discussed in § 6 (ii) (see Room, unpublished, part 3).

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Solar radiation in the radio spectrum

I. Radiation from the quiet sun

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The theory of the emission of thermal radiation from the solar envelope at radio-frequencies is worked out in detail. The Lorentz theory of absorption is used in conjunction with Kirchhoff's law to derive the effective temperature of the various regions of the solar disk over the radio spectrum. A maximum effective temperature approaching 10^6 °C is found in the vicinity of 1 m. wave-length. Limb brightening occurs at centimetre wave-lengths. It is shown that Gaunt's quantum mechanical expression for free-free emission yields results almost identical with the classical treatment, provided Chapman and Cowling's expression for the collision frequency in a fully ionized gas is used in the latter treatment. It is suggested that it may be preferable to treat problems of solar and galactic radio noise by classical methods, particularly when the refractive index of the medium departs appreciably from unity.

1. INTRODUCTION

The great advances in radio technique in the past few years have, theoretically, made it possible to detect solar radiation on wave-lengths of the order of centimetres. At such wave-lengths Planck's formula for black-body emission degenerates to the Rayleigh-Jeans formula, and the emissivity of a black body becomes proportional to $T\lambda^{-2}$ per unit frequency increment, T being the temperature of the source, and λ the wave-length of the radiation. The first successful observations of such emission from the sun appear to have been made by Reber (1944) and Southworth (1944). The latter deduced from his observations a value of T about 6000° C at a wave-length of about 10 cm., agreeing with the well-known temperature found in the visible region of the spectrum. Subsequently, however, Southworth (1946) corrected his results and deduced a temperature of 20,000° C.

In the meantime, a number of investigators, notably Appleton (1945), and Pawsey, Payne Scott & McCready (1946), had reported strong but variable emission from the sun at considerably longer wave-lengths, of the order of metres. Appleton, and also Pawsey *et al.*, suggested that such emissions, which appeared to correlate with sunspots, could not well be thermal in character, since such an interpretation would require the postulation of impossibly high values of T on the sun.

This paper (I) is concerned only with the discussion of that component of solar radiation which appears to be thermal in origin. It is hoped to discuss the more highly organized radiation which appears to be correlated with sunspots in part II.

The recent investigations of Edlén (1942) and Alfvén (1941) have shown that coronal matter is normally at a temperature approaching one million degrees. It is obviously important, therefore, in interpreting the observations, to have a clear picture of the region of the sun (photosphere, chromosphere or corona) from which the observed radiation at any selected wave-length is emitted. To achieve this, a reasonably accurate knowledge of the electron-pressure distribution in these regions is necessary. Fortunately, such information is available from several sources. Baumbach (1937) gives what should be reliable estimates of the electron densities in the corona, since they are deduced directly from observations of light scattering by these particles. Cillié & Menzel (1935) have made a theoretical investigation of the electron pressures in the chromosphere. It was found in the course of the present investigation that radiation in the radio spectrum does not originate in regions lower than this.

2. RADIATION FROM AN ELECTRON-ION ATMOSPHERE

The problem of the depth from which solar radiation of given frequency issues has already been encountered by solar physicists. Milne has introduced the useful concept of optical depth τ given by $\tau = \int \kappa ds$, where κ is the absorption coefficient and ds an element of path along the selected ray. He has shown (Milne 1930) that the radiation observed from a slab of material comes from an average optical depth $\tau = 1$ measured along the ray. This concept is adequate for conditions encountered in the visible spectrum. It is found below, however, that over a large part of the radio spectrum the refractive index μ of the medium is considerably less than unity. Moreover, the electron-collision frequency ν is so small that it is possible at certain wave-lengths for incoming radiation to penetrate the solar envelope to the level $\mu = 0$ without serious absorption. In other words, at certain (radio) wave-lengths the solar envelope is a reflector. Under such conditions it may be impossible for incoming radiation to reach the optical depth unity with appreciable intensity, and Milne's criterion cannot be applied.

It is a well-known fact in the theory of radio propagation in the ionosphere that under these circumstances most of the absorption occurs near the level $\mu = 0$, where the ray is strongly deviated (by angle π for the presently assumed case of vertical incidence). It will be sufficient then to replace Milne's criterion in such cases by the criterion that the observed radiation comes from the level $\mu = 0$. In these cases, however, the radiation emitted at wave-length λ will no longer be the full radiation corresponding to the temperature T at this level. Since the medium is a reflector it will be necessary, in calculating the emission, to reduce the theoretical black-body emission by a factor which is the absorptive power, in accordance with Kirchhoff's law. Those familiar with the theory of radio propagation in the ionosphere will readily recognize the distinction between the two cases described above. Milne's criterion applies for 'absorption in the non-deviating region'. The other treatment must be used for 'absorption in the deviating region'.

2.1. *The determination of the effective levels of emission*2.1.1. *Case (a). The atmosphere is a full absorber*

For this class of wave-lengths, which lies at the short-wave end of the radio spectrum, it is necessary, as explained above, to determine the levels at which $\tau = 1$. Baumbach's results (1937), which are described below, reveal that the electron-density gradient in the corona is exponential in form. Moreover, it is found that the exponential coefficient is constant over large ranges of radial distance from the sun. Since the corona is completely ionized and neutral, ν must also have an exponential gradient, with approximately the same coefficient, so long as the temperature change is small over the range under consideration.

Hence

$$N = N_0 e^{-\beta r}$$

and

$$\nu = \nu_0 e^{-\beta r},$$

where N is the electron density at distance r from the sun's centre, and N_0 , ν_0 , β are constants to be determined later from Baumbach's results.

Absorption of a ray in a medium of this type has been previously worked out (Martyn 1935*a*). From the latter treatment* it follows immediately that

$$\tau_{r,i} = \frac{2\nu_0 p^2 \cos^3 i}{3c\beta\rho N_0} \{2 - \sin\theta(2 + \cos^2\theta)\},$$

where

$$\cos^2\theta = \rho N/p^2 \cos^2 i,$$

i being the angle of incidence of the ray, $p/2\pi$ the wave frequency, c the velocity of light, and $\rho = 4\pi e^2/m$, e , m being the electronic charge and mass. Writing ' a ' for $3c\beta\rho N_0/2\nu_0 p^2 \cos^3 i$, the condition for $\tau = 1$ is

$$\sin^3\theta - 3\sin\theta + (2-a) = 0. \quad (1)$$

The solution of this cubic equation gives the value N' of N at which $\tau = 1$, when the frequency and angle of incidence are specified. Over most of the range to be investigated it turns out that $a \ll 1$. In these circumstances the solution of equation (1) is

$$\cos^2\theta = 1.15\sqrt{a},$$

and so

$$N' = 1.15p \cos^{\frac{1}{2}} i \sqrt{(3c\beta N_0/2\rho\nu_0)}. \quad (2)$$

2.1.2. *Case (b). The atmosphere is a partial reflector*

In these cases, which apply for the longer wave-lengths and shallower angles of incidence, the level at which an incoming ray is turned back has to be determined, since this is the region where absorption chiefly occurs. This level is readily fixed by an application of Snell's law, together with the well-known expression due to Lorentz for the refractive index of an ionized gas, viz.

$$\mu^2 = 1 - \rho N/p^2.$$

* In the paper quoted, absorption was expressed in ratios of electric field strength. In the present paper it is expressed in energy ratios, in accordance with optical convention.

At the turning point, by Snell's law,

$$\mu_1^2 = \sin^2 i = 1 - \rho N_1/p^2,$$

and so

$$N_1 = p^2 \cos^2 i / \rho. \quad (3)$$

For given p and i equation (3) determines the level from which the radiation is principally emitted, when the atmosphere is a reflector.

2.2. *The determination of the absorptive power of the medium*

The absorptive power A of the medium is, by definition, $(1 - e^{-2\tau_1})$, where τ_1 is the optical depth of the turning point of an incoming ray. Clearly, for wave-lengths such that the medium is a full absorber, A is unity.

When the medium has appreciable reflecting power it is necessary to know τ_1 , in order to calculate the emission by Kirchhoff's law. It has previously been shown (Martyn 1935*a*) that for a medium with exponential gradient

$$\tau_1 = 4\nu_0 \cos^3 i p^2 / 3c\rho\beta N_0. \quad (4)$$

2.3. *The effect of a magnetic field on the emission levels*

2.3.1. *The absorption levels*

When the presence of a magnetic field H is taken into account the atmosphere becomes doubly refracting, and for each frequency there are two levels of effective absorption. The appropriate theory for a uniformly ionized medium has been given by Appleton (1932). The equations expressing the two modes of propagation (the 'ordinary' and 'extraordinary' rays) are cumbersome, but fortunately it has proved possible to make adequate approximations for the purposes of this paper. In particular, the fact that $\nu/p \ll 1$ over the region of the radio spectrum under examination greatly simplifies the equations. Another simplification arises from the fact that the gyro-frequency $\omega (= He/m)$ is found to be less than p in the absorbing regions of the solar envelope, if H be given the value appropriate to the sun's general magnetic field.

Over all but a very limited range of values of i the treatment given in (2.1.1) and (2.1.2) remains valid for the ordinary ray. For the extraordinary ray, however, it becomes necessary to replace ' a ' in equation (1) by $a(1-y)/(1-|y_L|)$, where y is ω/p , and y_L is the component of y along the direction of the ray, and to put

$$\cos^2 \theta = \rho N/p^2(1-y) \cos^2 i.$$

(The basis of these approximations is due to Booker (1935).) Over most of the range to be investigated an approximation similar to equation (2) is valid for the extraordinary ray. Thus

$$N'' = 1.15(1-y)^{\frac{1}{2}}(1-y_L)^{\frac{1}{2}} p \cos^{\frac{1}{2}} i / \sqrt{(3c\beta N_0/\rho\nu_0)}. \quad (5)$$

This gives, for the extraordinary ray, the value of N for which $\tau = 1$.

When the atmosphere is a reflector a treatment similar to that in (2.1.2) gives

$$N_2 = p^2 \cos^2 i (1 \pm y) / \rho, \quad (6)$$

the minus sign applying when $p > \omega$, and the plus when $p < \omega$. A complication occurs in these cases, as compared with the ordinary ray, N being no longer simply proportional to p or p^2 . This complication is usually unimportant in equation (5), since it turns out that for a wide range of the high frequencies here involved $y \ll 1$, so long as H has the magnitude appropriate to the sun's general magnetic field. For the lower frequencies involved in equation (6), however, y is found to be of the order of 0.5, and it becomes necessary to solve the equation rigorously as a quadratic in p , bearing in mind that ω and N are functions of r , the distance from the sun's centre.

The solution of equation (6) is

$$2p = \mp \omega \pm \sqrt{(\omega^2 + 4\rho N_2 / \cos^2 i)},$$

in which the plus and minus signs may be taken in any combination. Clearly, however, the negative sign before the radical must be discarded as it can only lead to negative solutions. This leaves two possible solutions for p . It turns out that for the values of N and ω appropriate to the corona and chromosphere (§ 3 below) both solutions give $p > \omega$ at all levels. This rules out the use of the minus sign in front of ω . The only* valid solution is then

$$2p = \omega + \sqrt{(\omega^2 + 4\rho N_2 / \cos^2 i)}.$$

This result is particularly satisfactory, as the approximation involved in equation (6) is rather crude when $y > 1$.

In practical computing a series of values of r are selected, N and ω being known for each value of r . Representative values of i (20, 40, 60, 80°) are taken, and equation (6) solved for p for each pair of values of r and i . By graphical interpolation the values of N_2 are then determined for any pair of values of p and i .

2.3.2. *The absorptive power of the medium*

From the discussion in (2.3.1) it follows that the optical depth τ_2 of the turning point for the extraordinary ray is given by

$$\tau_2 = 4\nu_0 \cos^3 i p^2 (1 - y) / 3c\rho\beta N_0 (1 - y_L). \quad (7)$$

2.4. *The validity of the application of Kirchhoff's law to a magnetically anisotropic medium*

In proving his law, Kirchhoff made use of the reciprocity theory of Helmholtz. It is well known that theorems of this type break down when applied to magnetically anisotropic media. It seems desirable therefore to examine carefully the application of Kirchhoff's law to the solar envelope in the manner propounded in the present paper. The proper application of the law requires the specification of the plane of polarization.

* This conclusion differs from that of Saha (1946), who considers that both signs are permissible when $p > \omega$. Most workers, including the present author, appear to consider that heavy absorption prevents the occurrence of the second extraordinary component in such cases.

Consider a beam of radiation plane polarized in a direction x at right angles to the direction of propagation, and let it be incident upon the medium with an amplitude $E \sin pt$. Let y be another direction at right angles to x and to the direction of the beam. The plane-polarized beam may be split up into two equal circularly polarized components having opposite senses of rotation, thus:

$$(i) \quad E_x = E/2 \cdot \sin \omega t, \quad E_y = E/2 \cdot \cos \omega t,$$

$$(ii) \quad E_x = E/2 \cdot \sin \omega t, \quad E_y = -E/2 \cdot \cos \omega t.$$

The first of these components may be considered to be propagated through the medium as the ordinary component, and the second as the extraordinary component.

When the medium varies sufficiently slowly in its properties (a condition which certainly is satisfied in the solar envelope), Booker (1936) has shown that these two components can preserve their identity, each emerging after refraction with a characteristic polarization. For conditions where $\nu \ll p > \omega$ this limiting polarization is very nearly circular for all but a very narrow range of angles between the emerging ray and the magnetic field direction (Martyn 1935*b*). Assuming circular polarization, the emerging intensities may be written as

$$(iii) \quad E_{x'} = \rho_1 E/2 \cdot \sin \omega t, \quad E_{y'} = \rho_1 E/2 \cdot \cos \omega t,$$

$$(iv) \quad E_{x'} = \rho_2 E/2 \cdot \sin \omega t, \quad E_{y'} = -\rho_2 E/2 \cdot \cos \omega t,$$

where ρ_1 and ρ_2 are the attenuations of the ordinary and extraordinary components respectively. The total average energy in the emerging ray is therefore proportional to

$$\{(\rho_1 + \rho_2)^2 + (\rho_1 - \rho_2)^2\} E^2/8 = (\rho_1^2 + \rho_2^2) E^2/4.$$

Since the average energy in the incident ray is similarly proportional to $E^2/2$ it follows that the absorptive power is

$$A = \frac{1}{2}\{(1 - \rho_1^2) + (1 - \rho_2^2)\}.$$

Expressing $\rho_{1,2}$, which are ratios of field intensities, in terms of optical depths, this becomes

$$A = \frac{1}{2}\{(1 - e^{-2\tau_1}) + (1 - e^{-2\tau_2})\}.$$

By Kirchhoff's law it can now be asserted that if the emissive power I of the medium be resolved into the two plane-polarized components I_x and I_y , then

$$I_x = \frac{1}{2}AB_f,$$

where B_f is the black-body emission at frequency f . Now A is clearly independent of the direction chosen for x , since it is a function only of the optical depths of the two independent *circularly* polarized components. It follows that

$$I_x = I_y \quad \text{and} \quad I = \frac{1}{2}B_f(A_1 + A_2),$$

where $A_{1,2}$ are the absorptive powers of the medium for the two components.

It seems clear that, for the particular conditions specified above, which result in the limiting polarizations being circular, Kirchhoff's law can be applied separately

to each component. The total emission will then be half the sum of the two unequal circularly polarized components so calculated.

It is satisfactory to note that Eckersley (1940) has experimentally verified the reciprocity theorem for conditions similar to those specified above. It seems likely, however, that the conclusions reached above would become invalid in cases where $p < \omega$ and the limiting polarizations of each component become markedly elliptical.

3. THE PHYSICAL CONDITIONS IN THE CHROMOSPHERE AND CORONA

For the theoretical deduction of thermal radiation from the solar envelope it is necessary to know the temperature distribution, the pressure distribution, the degree of ionization at the various levels, and the proportions of the constituent gases. Available knowledge regarding these quantities in the corona has been summarized recently (Alfvén 1941). Edlén's identification (1942) of the coronal lines as due to highly stripped metallic atoms leaves little doubt that the coronal matter is at a high temperature. Alfvén has supplied additional lines of reasoning, notably that of the large 'scale-height' of the electron atmosphere in the corona, which make it reasonably certain that the temperature approaches one million degrees in this region. Since the surface of the photosphere is at approximately 6000°C there must be a fairly sharp rise of temperature on passing through the chromosphere and inner corona. The observations of Redman (1942), who deduced kinetic temperatures in the chromosphere of order $30,000^\circ\text{C}$ from a study of spectral line profiles, now fall into place. The temperature distribution used in the present paper is based on Alfvén's work for the corona, and on Redman's observations for the chromosphere: it is given in figure 1.

The distribution of electron density is known from the work of Baumbach (1937), who has analyzed the coronal isophotes from a number of eclipses. Baumbach's results are shown also in figure 1. They do not extend, of course, so far inwards as the chromosphere, and here appeal is made to Cillié & Menzel's theoretical calculations (1935). The two sets of results have been joined smoothly, the junction occurring in the vicinity of $N = 4 \times 10^8$ electrons per c.c. It seems unlikely that Baumbach's results will be much modified by subsequent investigations, so long as it be remembered that they represent average conditions only. On the other hand, Cillié & Menzel took no account of the probable rise of temperature in the chromosphere, and their results may have to be modified subsequently. For the purposes of this paper the quantitative uncertainty here is probably unimportant.

The constituents can safely be assumed as a Russell mixture, viz. 28 parts of H,* 1 part of O type atoms, and 1 part of metals. At the coronal temperature the hydrogen must be fully ionized, O type six times ionized, and metals ten times ionized. The

* *Note added 22 January 1948.* Recent developments in solar physics suggest that the proportion of H may be much greater than here assumed. If this proves to be the case then the values of ν calculated below must be reduced by a factor between 1 and 5. This would produce only small displacements in the curves of figures 3 and 4.

contribution of each type of ion to the electron-collision frequency is shown below to be proportional to $n_1 e_1^2$, where n_1 is the number density of the ion, and e_1 its charge. Hence

H contributes	$28 \times 1 = 28$	} total 164.
O contributes	$1 \times 6^2 = 36$	
Metals contribute	$1 \times 10^2 = 100$	

It will be sufficient, therefore, to work out the electron-collision frequency with metallic ions and to increase the value obtained by two-thirds in order to allow for the presence of the other ions.

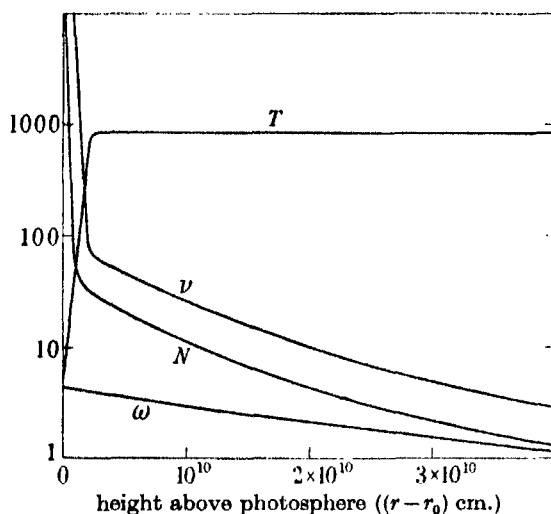


FIGURE 1. N , distribution of electron densities (number of electrons/c.c. $\times 10^{-7}$); ν , electron collision frequency (collisions/sec.); T , temperature ($^{\circ}\text{K} \times 10^{-3}$); ω , gyro-frequency (radians/sec. $\times 10^{-8}$), in corona.

Alfvén has given values of ν deduced by assuming a collision cross-section of 10^{-17} cm^2 . This does not take account of the fact, however, that the coronal matter is highly ionized, so that there are strong attractive forces between the electrons and heavy particles. The importance of this factor in the solar atmosphere has been stressed by Cowling (1945). It is readily deduced from the latter's work (equation (35), loc. cit.) taken in conjunction with that of Chapman & Cowling (1939) on this type of gas, that

$$\nu = \frac{2\sqrt{(2\pi)n_1 e^2 e_1^2}}{3m^{\frac{1}{2}}(kT)^{\frac{1}{2}}} A_1(2), \quad (8)$$

where

$$A_1(2) = \log_e \left\{ 1 + \frac{(4dkT)^2}{ee_1} \right\}.$$

k is Boltzmann's constant, and d is the mean distance between pairs of neighbouring ions and electrons. $A_1(2)$ is, therefore, a slowly varying function of temperature and pressure; it has the numerical values 25 in the corona, and 11 in the chromosphere.

It is of interest to compare the value of ν calculated from equation (8) for a given level in the corona, with that given by Alfvén for the same level. At the level $r = 7.71 \times 10^{10}$, figure 1 shows that $N = 1.55 \times 10^8 \text{ cm.}^{-3}$. The Russell mixture gives 44 electrons for one metallic ion, so that $n_1 = 3.52 \times 10^8 \text{ cm.}^{-3}$. Inserting the other numerical values in equation (8), it is found that $\nu = 20.4$ collisions per sec. This has to be increased by two-thirds to $\nu = 34$ per sec. in order to allow for the other types of ion present. This is to be compared with Alfvén's estimate, $\nu = 2.2$ per sec. at the same level. It is clear that neglect of the electrostatic forces is not permissible. The distribution of ν in the corona and chromosphere deduced in the above manner is shown in figure 1.

In calculating the absorption and locating the emission levels by equations (1), (2), (4) and (7) it will be observed that the solar variables appear always in the relationship $\beta N_0/\nu_0$. It is clear from equation (8) that N_0/ν_0 will vary markedly with T , so that this ratio will have very different values in the corona and chromosphere. The scale height $1/\beta$ varies, however, in such a way as to keep $\beta N_0/\nu_0$ roughly constant. Thus, the latter quantity is found to have the numerical values 2.4×10^{-4} in the outer corona, 5.6×10^{-4} in the inner corona, and 8×10^{-4} at the base of the chromosphere. The small variation of $\beta N_0/\nu_0$ over such a wide range of conditions is justification for the use of the simple formulae in equations (4) and (7) for computing the absorption over regions where β and N_0/ν_0 individually are changing appreciably.

There appears to be little doubt that the sun possesses a general magnetic field whose influence extends into the corona. The strongly suggestive appearance of the polar tufts in this connexion is now supported by measurement (Thiessen 1946). This investigator finds the polar value of H to be 50 gauss. The corresponding values of the gyro-frequency are shown in figure 1. In calculating these it has been assumed that the distribution of H in the solar atmosphere is similar to that in the earth's.

4. TREATMENT OF DATA

For the purpose of calculating the solar emission the disk of the sun was divided into four or more annuli. These were chosen so that the radiation received at the earth emerged at mean angles of 20, 40, 60 and 80° respectively to the solar radius. This leaves a small central disk for which i is approximately zero. For each frequency the levels from which the radiation emanated were determined by the use of equation (1). In the lower range of frequencies, as explained above, $\tau < 1$, and the appropriate levels were determined from equations (3) and (6). For high frequencies and small values of i (the inner annuli), it was usually possible to employ equations (2) and (5) instead of (1), thus greatly reducing the labour of computation.

The levels determined for a range of the lower frequencies are shown in figure 2 for the 'ordinary' and 'extraordinary' radiation respectively. At the largest value of i (80°) the results can only be rough, since towards the limb of the sun the approximation involved in treating the surfaces of the annuli as plane will break down. The

condition $\mu \sin i = \text{constant}$, used for ray tracing, should here be replaced strictly by $\mu r \sin i = \text{constant}$. It has not been thought necessary to treat this complication in the present paper.

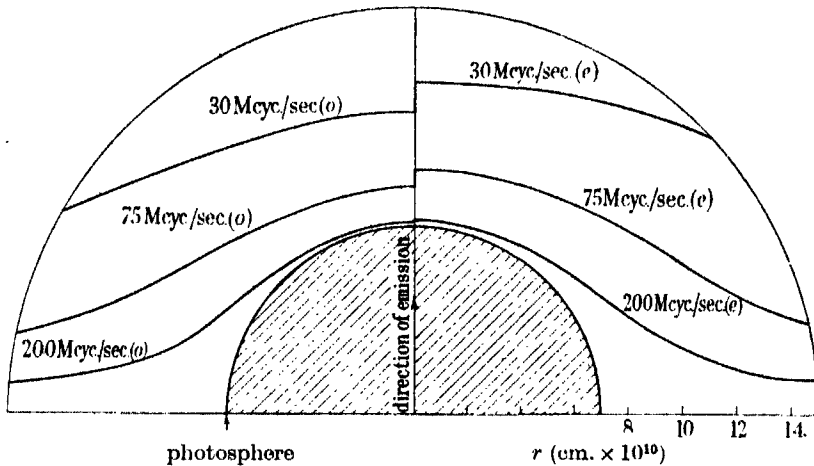


FIGURE 2. Coronal emission levels for solar radiation, ordinary (o) and extraordinary (e) at frequencies of 30, 75 and 200 Mcyc./sec.

The complete procedure in computing the radiation is now as follows. At the given frequency the average level from which the radiation emanates is determined for each annulus as described above. This determines the value of T for each annulus. When the level has been determined by the condition $\tau = 1$, then T is also the effective temperature T_e of this annulus, *considered as a full radiator* at the chosen frequency. For values of p and i which give $\tau < 1$ at this level, the absorptive power $(1 - e^{-2\tau})$ is computed from equation (1). In such cases, the effective temperature of the annulus considered as a full radiator becomes $T(1 - e^{-2\tau})$ by Kirchhoff's law.

Proceeding in this manner the values of T_e for a number of frequencies were computed for the ordinary radiation. The results are shown in figure 3 for various frequencies selected to illustrate all the typical distributions of T_e across the disk, within the radio spectrum. In figure 3, T_e is plotted, for each frequency, as a function of the distance from the centre of the solar disk. It should be noted that in this figure r_0 , the solar radius, has not necessarily the value measured by optical methods. The precise definition of r_0 would require a higher degree of approximation, at the glancing angles from the solar limb, than is used in this paper. It is observed that the lower frequencies show 'limb darkening', although, of course, this occurs for a physical reason quite different from that which explains the same phenomenon in the visible region of the spectrum. At wave-lengths in the neighbourhood of 1 m. the disk is uniformly bright, but at wave-lengths only slightly shorter, pronounced 'limb brightening' appears. This, of course, is due to the fact that the radiation in the middle of the disk is emanating from the chromosphere, which is at a much lower temperature than the corona. At the glancing angles from the limb the radiation still comes from the corona.

It is now an easy matter to compute for each frequency the average value of T_e over the whole disk. This was done by assigning to each annulus a weighting factor proportional to the projected area of the annulus perpendicular to the line of sight.

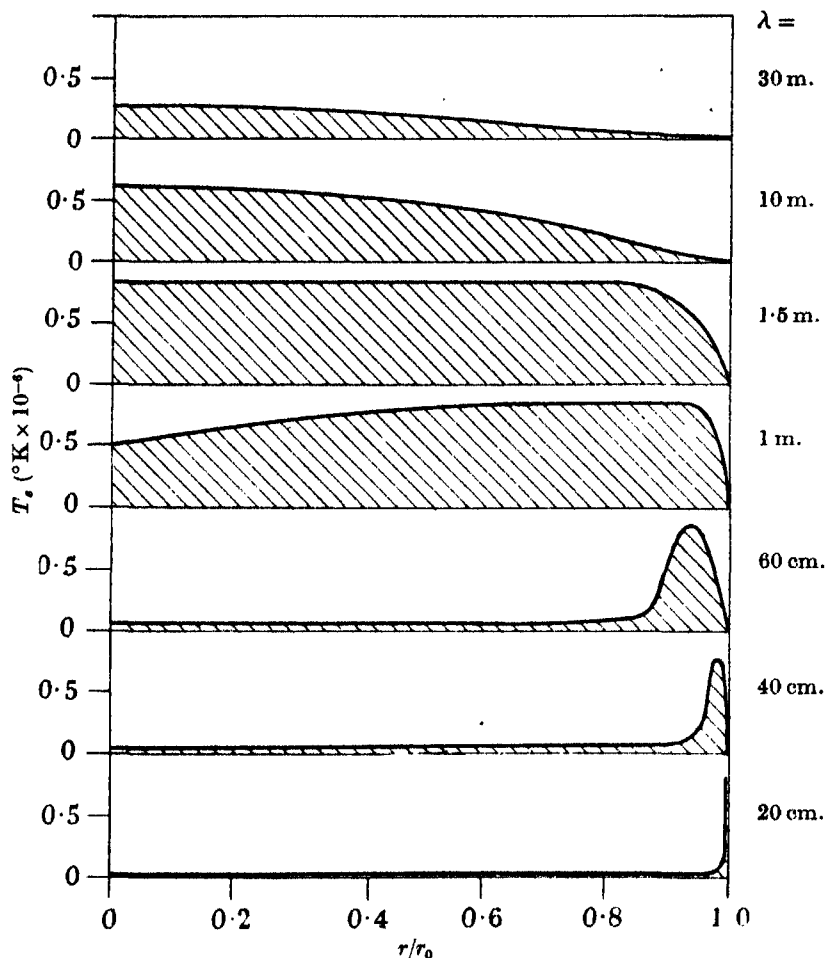


FIGURE 3. Variation of T_e across solar disk at various wave-lengths ($r = r_0$ at limb).

Figure 4 shows the resulting distribution of T_e for the range of frequencies under consideration. T_e is seen to have its maximum value at a wave-length of about 1 m.

The 'extraordinary' emission has been derived from the above computations of the ordinary emission by the following approximate treatment.

Consider first the higher frequencies where equation (2) is applicable to the ordinary radiation and equation (5) to the extraordinary. Since the solar envelope is a full radiator for these cases the only difference in emission arises from the different temperatures at the different emission levels for each component. At high frequencies ($\lambda < 10$ cm.) the accurate solution of equation (6) shows that $y \ll 1$ at the turning point. Since the level $\tau = 1$ is above this point, and ω decreases upward, it follows

that $y \ll 1$ at the level of emission. The ordinary and extraordinary radiations are therefore equal at such frequencies. For wave-lengths of 1 m. and upwards, accurate solution of equation (6) shows that y varies very little from the value 0.5. A weighted average value for y_L over the disk at $\lambda = 1$ m. is about 0.17. Hence $(1-y)^{\frac{1}{2}}(1-y_L)^{\frac{1}{2}}$ is 0.65. The extraordinary emission at frequency p is therefore equal to the ordinary emission at frequency $0.65p$. For the lower frequencies ($\lambda > 1$ m.) the temperature at the emission levels for the ordinary and extraordinary radiation are practically the same, but the emission differs because of the different absorption coefficients expressed in equations (4) and (7). Proceeding in a manner similar to that described in the preceding paragraph it can readily be shown that the extraordinary emission at frequency p is equal to the ordinary at frequency $0.77p$. In this manner the extraordinary radiation has been derived from the previously computed ordinary radiation. It is shown by the dashed line in figure 4.

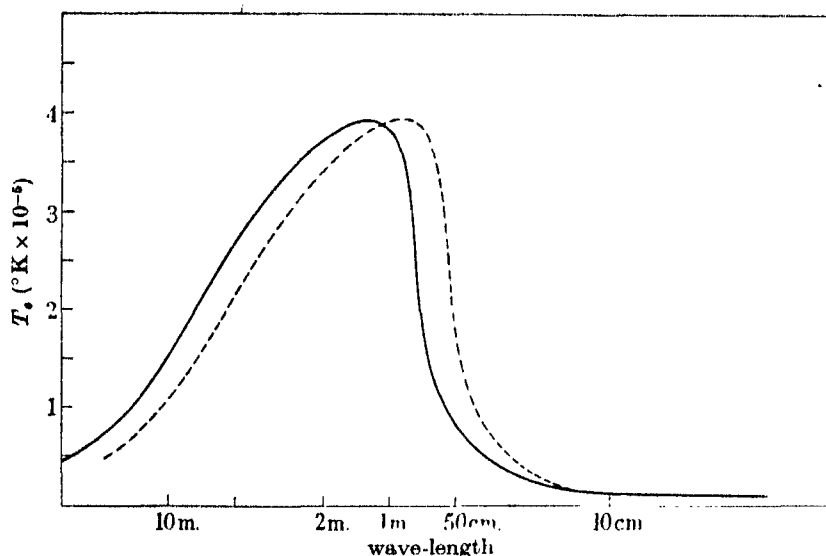


FIGURE 4. Effective temperature of the sun considered as a full radiator, in the radio spectrum, for the ordinary and extraordinary components. The total emission at wave-length λ is proportional to $[T_e(\text{ord.}) + T_e(\text{extraord.})] \times \lambda^{-2}$. ——— Ordinary radiation, - - - - extraordinary radiation.

5. COMPARISON OF THEORETICAL RESULTS WITH OBSERVATIONS

The value of T ($20,000^\circ$) at 10 cm. measured by Southworth (1944) appears to lie on the theoretical curve of figure 4. At a wave-length of 1.5 m. Pawsey (1946) finds a background of noise which he interprets as thermal radiation corresponding to $T = 10^6$ degrees. Dicke & Beringer (1946) found $T = 10^4$ degrees at 1 cm. All these results agree satisfactorily with the theoretical curve in figure 4. Similar observations at wave-lengths near 50 cm. would be of considerable value in testing the theory. At the longer wave-lengths (> 1 m.) it may prove difficult to separate the thermal radiation from that associated with sunspots.

Observations of the variation of brightness across the solar disk would provide a valuable test of the theory. Covington (1947) has studied the effect of the partial solar eclipse of 23 November 1946 on solar noise at a wave-length of 10.7 cm. When the radiation from an active spot group has been eliminated from his results it appears that the curve of diminution of noise during the eclipse is considerably shallower than would be expected theoretically if the noise emanated uniformly from the disk. There is also some evidence of an unexpected large drop in intensity near first contact. Both these results are to be anticipated if the above conclusions regarding limb brightening at such wave-lengths are correct.*

6. RADIATION DEDUCED FROM KIRCHHOFF'S LAW COMPARED WITH THAT FROM THE THEORY OF FREE-FREE TRANSITIONS

Reber (1940) interpreted galactic radio radiation as due to free-free transitions of electrons in the field of protons in interstellar space. This idea was further developed by Henyey & Keenan (1940), and has been applied to solar radio noise by Greenstein (1947). The latter has expressed doubts about the validity of the Kirchhoff treatment (Martyn 1946), which is used also in the present paper, and advances arguments tending to show that thermal solar radiation will not decrease at low frequencies as is indicated in figure 4.

Since the problem is essentially a classical one ($hf \ll kT$), the correspondence principle should apply, and both treatments should give almost identical results. The present section is devoted to testing this point, and to a consideration of the relative advantages of the two treatments for calculating emission.

The classical absorption coefficient κ used in the present paper is due to Lorentz and is given by

$$\kappa = \frac{\nu}{c\mu} \frac{Ne^2}{\pi m f^2}. \quad (9)$$

This expression for κ has been used in the present paper to describe absorption of energy both in the deviating region ($\mu \ll 1$) and in the non-deviating region ($\mu \doteq 1$). Workers who have applied quantum mechanics to the problem do not appear to have yet considered media where N is large enough to cause μ to depart appreciably from unity, so, for comparison with their results, μ is put equal to 1. A neutral electron-proton gas is considered. In the above expression for κ , ν is now eliminated by the use of equation (8). This equation is valid only for binary encounters, and for an electron-proton gas it is readily verified that under such conditions $\frac{(4dkT)^2}{e^2} \ll 1$, and $d \doteq 1/(2N)^{\frac{1}{2}}$. Hence

$$\kappa \text{ (Lorentz, Chapman)} = \frac{4\sqrt{2} N^{\frac{3}{2}} e^6}{3\sqrt{\pi} c (mkT)^{\frac{1}{2}} f^2} \log_e \left\{ \frac{4kT}{e^2 (2N)^{\frac{1}{2}}} \right\}. \quad (10)$$

* Results similar to Covington's, for another eclipse, have just been reported by Sander (*Nature*, 12 April 1947), who considers that they show limb brightening.

The above expression has been derived on purely classical lines from simple considerations of the absorption of a *plane* wave due to collisions (Lorentz), combined with Chapman & Cowling's first approximation to the diffusion coefficient in a fully ionized gas. In comparing it with that derived by quantum mechanical methods it is necessary to give precision to the definitions of intensity of radiation, etc., and to consider carefully the form of the radiation field. For this purpose, the definitions and terminology used by Milne (1930) are followed throughout. The equation of transfer of radiation can be written (Milne 1930, p. 161) as

$$\frac{dI_f}{ds} = -n'I_f + \frac{q'}{q''}n''(\sigma + I_f), \quad (11)$$

where α_f is the absorption coefficient of an electron-proton pair in the state f , I_f is the intensity of radiation, ds is an element of path along the direction considered, n' , n'' are the numbers of ion pairs per c.c. in the absorbing and emitting states respectively, and q' , q'' are the statistical weights of these two states, and $\sigma = 2hf^3/c^2$.

This equation is to be compared with that derived on the simple Kirchhoff theory, viz.

$$\frac{dI_f}{ds} = -\kappa I_f + \kappa B_f. \quad (12)$$

(This simply expresses the fact that the gain of intensity along the pencil of radiation is the difference between the intensities emitted and absorbed.)

For comparison with the classical absorption coefficient it is clear that κ is the quantity to be determined. For when plane waves are considered $I \gg B$ (I becomes infinite along the direction of propagation of a plane wave, but this, of course, presents no difficulty in practice, since such a wave is physically unrealizable). Hence, for plane, or nearly plane, waves, the solution of equation (12) becomes

$$I_f = I_f^0 e^{-\kappa s},$$

showing that κ is the quantity to be compared with the Lorentzian absorption coefficient. For conditions of local thermodynamic equilibrium equations (11) and (12) must be identical, so that

$$\kappa = \alpha_f(n' - n''q'/q'').$$

But by Boltzmann's equation

$$\frac{n''}{n'} = \frac{q''}{q'} e^{-hf/kT},$$

so that

$$\kappa = n'\alpha_f(1 - e^{-hf/kT}). \quad (13)$$

Now, $n'\alpha_f$, when summed over all the (continuous) absorbing states, is the true absorption coefficient of the medium. At radio-frequencies, however, the quantity in round brackets in equation (13) is very small (about 10^{-7}), so that κ is very much smaller than the true absorption coefficient. The physical significance of this is clear. At these frequencies, the Einstein stimulated emission is much larger than the spontaneous emission. Moreover, as Dirac (1926) has pointed out, the stimulated

emission must have the same direction as the stimulating field. Hence, at radio-frequencies, the effective absorption coefficient is very much less than the true absorption coefficient, owing to the presence of the large stimulated field.

The emission from the encounter of electrons and protons was first calculated by Kramers (1923) on classical lines. Cillié (1932) gave a quantum treatment. The latter's expression for the total emission is

$$\frac{2^7 \pi^3 N^2}{(6\pi)^{\frac{1}{2}}} \left(\frac{m}{kT} \right)^{\frac{1}{2}} \frac{e^6}{c^3 m^2} e^{-hf/kT} df / \text{c.c./sec.}$$

This must be divided by 4π in order to obtain the intensity of emission E_f . The later wave-mechanical treatment of Gaunt (1930) adds a correction factor g , given by

$$g \doteq \frac{\sqrt{3}}{\pi} \log_e (3kT/2hf).$$

There has been some controversy whether the above expression for E_f includes the stimulated emission. Eddington (1923) has argued that it does, but Gaunt advances powerful reasons to the contrary. It will be found below that agreement between the classical and quantum treatments of the present problem is possible only if Gaunt's view is correct.

Assuming the latter viewpoint, the intensity of the unstimulated emission can be written as

$$E_f = \frac{\sqrt{3} 2^5 \pi N^2}{(6\pi)^{\frac{1}{2}}} \left(\frac{m}{kT} \right)^{\frac{1}{2}} \frac{e^6}{c^3 m^2} e^{-hf/kT} \log_e \left(\frac{3kT}{2hf} \right). \quad (14)$$

$$\text{But, by equation (11),} \quad E_f = \alpha_f \frac{q'}{q''} n'' \sigma = n' \alpha_f e^{-hf/kT} \frac{2hf^3}{c^2}. \quad (15)$$

Hence, by equations (13), (14) and (15), and remembering that $hf/kT \ll 1$

$$\kappa (\text{Kramers, Gaunt}) = \frac{4\sqrt{2} N^2 e^6}{3\sqrt{\pi} c (mkT)^{\frac{1}{2}} f^2} \log_e (3kT/2hf). \quad (16)$$

The agreement between the classical and the quantum expressions for κ is clearly very close, as it should be. The absorption coefficients are identical save that the slowly varying function $\log_e (4kT/e^2(2N)^{\frac{1}{2}})$ arising from the kinetic theory of an electron-proton gas, is replaced by the slowly varying function $\log_e (3kT/2hf)$ which arises from the Gaunt correction factor. Over the range of gas pressures, and radio-frequencies which are concerned in observations of galactic and solar radio noise, the ratio of these functions differs little from unity. Both formulae must break down at high densities, when encounters can no longer be considered as binary. The Lorentz-Chapman formula must break down also at very low densities and high frequencies since the Lorentz theory applies only when there are large numbers of electrons in a cubic wave-length. Over the range of conditions discussed in the present paper either treatment can be used. There are many advantages, however, in the use of the macroscopic concepts such as refractive index and absorption

coefficient which are employed in the present paper. Since conditions are encountered where $\mu \ll 1$, any theory based entirely on atomic concepts would have to consider the combined effect of the scattered field from the assemblage. It would seem to be unnecessary to proceed in this manner in dealing with a classical problem for which classical methods are adequate and relatively simple.

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A possible mode of propagation of the 'slow' or tail component in atmospherics

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In this paper a possible surface wave mode of propagation for the slow or tail component in an atmospheric is discussed. Surface wave solutions for the propagation of electromagnetic waves between infinite plane conductors are set up and it is shown that if one of the layers is of finite conductivity there is a solution which corresponds qualitatively with the observed velocities and periods of the slow component.

1. INTRODUCTION

Oscillograms of atmospherics show three distinct phases (a) a leader process, (b) an 'oscillatory' component and (c) a 'slow' component. (Appleton & Chapman 1937; Watson-Watt, Herd & Lutkin 1937.) In night atmospherics the oscillatory component takes the form of a series of pulses (Schonland, Elder, Hodges, Phillips & van Wyk 1940, figure 1, p. 185), and it has been shown (*loc. cit.*) that, as was originally suggested by Laby *et al.* (1937), these pulses represent reflexions from an ionospheric layer at a height of approximately 90 km.

For daylight atmospherics the pulses merge and the atmospheric appears as a damped wave train of gradually increasing wave-length (see figure 1). Nevertheless the spacing of the waves conforms to the formula given by Laby for ionospheric reflexions from a layer at a height of about 60 km. (Schonland *et al.* 1940, p. 202).

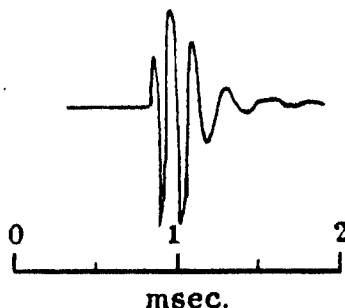


FIGURE 1. Typical daylight atmospheric.

The slow component does not fit into this picture and Dr Schonland suggested to me in 1939 that it was possible that the slow component was propagated as a surface wave. It is the purpose of this paper to discuss this suggestion.

2. OBSERVATIONAL MATERIAL

The observational material used in the discussion of the oscillatory component in § 4 consisted of oscillograms of daylight atmospherics recorded by Schonland and his associates. The distances were determined from direction finder (D.F.) observations at Johannesburg and Durban. Comparatively few records of the slow component were obtained, possibly because the amplifiers were not effective at the frequencies of 100 to 500 cycles characteristic of this component. For the slow component reference must be made to the paper by Watson-Watt *et al.* (1937). (References to the figures of this paper will be prefixed by W., e.g. W. figure 1.) For the discussion in § 6, a knowledge of the velocity-frequency relation is desirable. This is not directly available but W. figure 10 gives (a) the duration of the first half-cycle, and (b) the interval between the times of arrival of the oscillatory and slow components, plotted against distance. These two curves are reproduced as figure 2 of the present paper. In addition W. figure 7, reproduced (with some additions) as figure 3, gives a scatter diagram of the interval between the times of arrival plotted against distance.

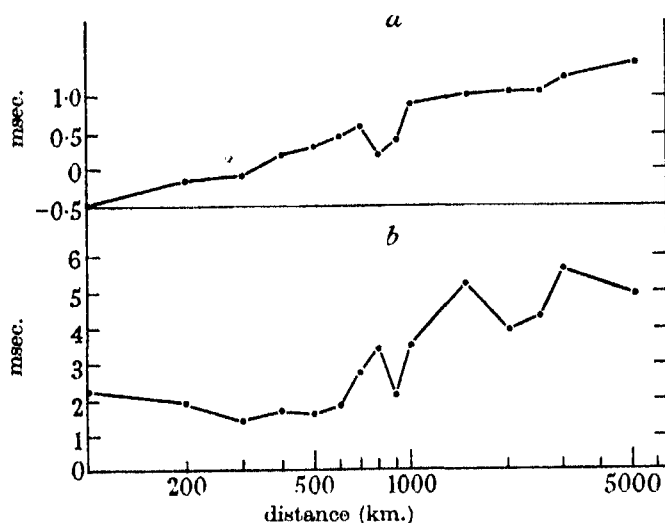


FIGURE 2. *a*, Interval between oscillatory and slow components (msec.) and *b*, duration of first half-cycle of slow component (msec.) as functions of the distance (Watson-Watt *et al.* 1937).

These figures will be discussed in greater detail in § 6. For the present it may be noted that the length of the first half-cycle varies from about 1.5 to 6 msec., and that, assuming that the onset of the oscillatory component travels with the velocity of light, the velocity of the slow component, estimated from the observations at 4000 km., ranges from $c/1.1$ to $c/1.3$.

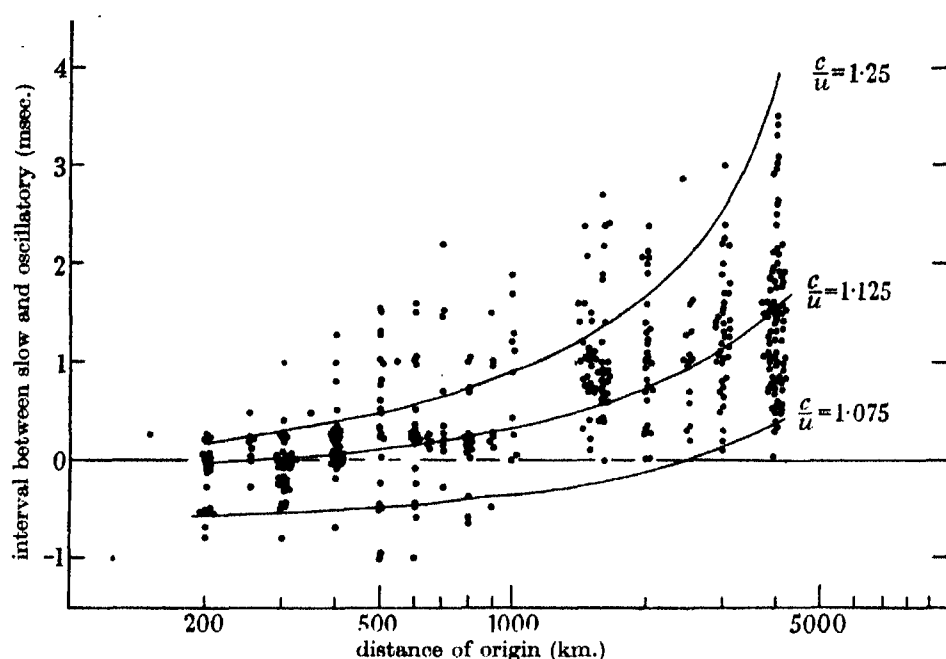


FIGURE 3. Scatter diagram of interval between the oscillatory and slow components (Watson-Watt *et al.* 1937).

3. GENERAL THEORY

Watson (1918) has given a complete solution of the problem of the propagation of electromagnetic waves between two media, either perfectly conducting, or with finite conductivity. This solution is more general than, and should include, those given below. Before this reference was found, however, the surface wave solutions given here had been set up and it is thought that they are more convenient than the general solution for the calculation of group velocities.

In Gaussian units the Maxwellian equations are

$$\frac{1}{c} \left(\epsilon \frac{\partial}{\partial t} + 4\pi\sigma \right) \mathbf{E} = \text{curl } \mathbf{H}, \quad (3.1)$$

$$\text{div } \mathbf{E} = 0, \quad (3.2)$$

$$-\frac{\mu}{c} \frac{\partial \mathbf{H}}{\partial t} = \text{curl } \mathbf{E}, \quad (3.3)$$

$$\text{div } \mathbf{H} = 0, \quad (3.4)$$

μ will be taken to be unity for the earth, atmosphere, and ionosphere. The effect of the curvature of the earth will be neglected and the direction of propagation taken as the axis of x , the z axis being vertical. The solutions sought are such that

the amplitude decreases exponentially with distance from the interface in the earth and ionosphere, and is a sine or cosine function of z in the atmosphere. In general there are two independent solutions of this type, namely (a factor $e^{i\omega(t-x/v)}$ has been omitted throughout):

(a) Vertical polarization

$$\left. \begin{aligned} E_{0x} &= A_0 e^{s_0 z}, \\ E_{0y} &= 0, \\ E_{0z} &= \frac{i A_0 \omega}{s_0 v} e^{s_0 z}, \end{aligned} \right\} \quad (3.5)$$

$$\left. \begin{aligned} H_{0x} &= 0, \\ H_{0y} &= \frac{i A_0 c}{\omega s_0} (s_0^2 - \omega^2/v^2) e^{s_0 z}, \\ H_{0z} &= 0, \end{aligned} \right\} \quad (3.6)$$

provided that
$$p_0^2 \omega^2/c^2 = \omega^2/v^2 - s_0^2. \quad (3.7)$$

$$\left. \begin{aligned} E_{1x} &= A_1 \sin s_1 z + B_1 \cos s_1 z, \\ E_{1y} &= 0, \\ E_{1z} &= \frac{i\omega}{s_1 v} (-A_1 \cos s_1 z + B_1 \sin s_1 z). \end{aligned} \right\} \quad (3.8)$$

$$\left. \begin{aligned} H_{1x} &= 0, \\ H_{1y} &= \frac{ic}{s_1 \omega} (A_1 \cos s_1 z - B_1 \sin s_1 z) (s_1^2 + \omega^2/v^2), \\ H_{1z} &= 0, \end{aligned} \right\} \quad (3.9)$$

provided that
$$p_1^2 \omega^2/c^2 = \omega^2/v^2 + s_1^2. \quad (3.10)$$

$$\left. \begin{aligned} E_{2x} &= A_2 e^{-s_2 z}, \\ E_{2y} &= 0, \\ E_{2z} &= -\frac{i A_2 \omega}{s_2 v} e^{-s_2 z}, \end{aligned} \right\} \quad (3.11)$$

$$\left. \begin{aligned} H_{2x} &= 0, \\ H_{2y} &= -\frac{i A_2 c}{\omega s_2} (s_2^2 - \omega^2/v^2) e^{-s_2 z}, \\ H_{2z} &= 0, \end{aligned} \right\} \quad (3.12)$$

provided that
$$p_2^2 \omega^2/c^2 = \omega^2/v^2 - s_2^2, \quad (3.13)$$

where p^2 has been written for $\epsilon - 4\pi i\sigma/\omega$, and the suffixes 0, 1 and 2 refer respectively to the earth, atmosphere and ionosphere.

(b) Horizontal polarization

$$\left. \begin{aligned} E_{0x} &= 0, \\ E_{0y} &= C_0 e^{s_0 z}, \\ E_{0z} &= 0, \end{aligned} \right\} \quad (3.14)$$

$$\left. \begin{aligned} H_{0x} &= -\frac{iC_0 c s_0}{\omega} e^{s_0 z}, \\ H_{0y} &= 0, \\ H_{0z} &= \frac{C_0 c}{v} e^{s_0 z}, \end{aligned} \right\} \quad (3.15)$$

subject to the condition (3.7).

$$\left. \begin{aligned} E_{1x} &= 0, \\ E_{1y} &= C_1 \sin s_1 z + D_1 \cos s_1 z, \\ E_{1z} &= 0, \end{aligned} \right\} \quad (3.16)$$

$$\left. \begin{aligned} H_{1x} &= -\frac{i c s_1}{\omega} (C_1 \cos s_1 z - D_1 \sin s_1 z), \\ H_{1y} &= 0, \\ H_{1z} &= \frac{c}{v} (C_1 \sin s_1 z + D_1 \cos s_1 z), \end{aligned} \right\} \quad (3.17)$$

subject to the condition (3.10).

$$\left. \begin{aligned} E_{2x} &= 0, \\ E_{2y} &= C_2 e^{-s_2 z}, \\ E_{2z} &= 0, \end{aligned} \right\} \quad (3.18)$$

$$\left. \begin{aligned} H_{2x} &= \frac{i C_2 c s_2}{\omega} e^{-s_2 z}, \\ H_{2y} &= 0, \\ H_{2z} &= \frac{C_2 c}{v} e^{-s_2 z}, \end{aligned} \right\} \quad (3.19)$$

subject to the condition (3.13).

The boundary conditions are that the tangential components of electric and magnetic force are continuous. These conditions lead to the equations of consistency.

(a) Vertical polarization

$$\tan s_1 h = \frac{p_0^2 s_0 + p_0^2 s_2}{p_0^2 p_1^2 s_1^2 - p_1^4 s_0 s_2} s_1 p_1^2, \quad (3.20)$$

(b) Horizontal polarization

$$\tan s_1 h = \frac{s_1 (s_0 + s_2)}{s_1^2 - s_0 s_2}, \quad (3.21)$$

where h is the height of the ionosphere.

Equations (3.20), (3.7), (3.10) and (3.13) can be solved to find v in terms of ω . In general the solutions must be carried out numerically and thus it is desirable to express the equations in forms which do not involve h explicitly. In addition p^2 for the atmosphere will be put equal to 1.

$$\text{Substituting} \quad s = \frac{\omega\alpha}{c}, \quad (3.22)$$

$$\gamma = \frac{c}{\omega h} = \frac{c\tau}{2\pi h}, \quad (3.23)$$

$$(3.7), (3.10) \text{ and } (3.13) \text{ become} \quad \alpha_0^2 = 1 - p_0^2 - \alpha_1^2, \quad (3.24)$$

$$\alpha_2^2 = 1 - p_2^2 - \alpha_1^2, \quad (3.25)$$

$$\frac{c^2}{v^2} = 1 - \alpha_1^2, \quad (3.26)$$

$$\text{and } (3.20), (3.21) \quad \tan \frac{\alpha_1}{\gamma} = \frac{p_2^2 \alpha_0 + p_0^2 \alpha_2}{p_0^2 p_2^2 \alpha_1^2 - \alpha_0 \alpha_2} \alpha_1, \quad (3.27)$$

$$\tan \frac{\alpha_1}{\gamma} = \frac{\alpha_1(\alpha_0 + \alpha_2)}{\alpha_1^2 - \alpha_0 \alpha_2}. \quad (3.28)$$

4. EARTH AND IONOSPHERE PERFECTLY CONDUCTING

If the earth and the ionosphere are assumed to be perfectly conducting both (3.27) and (3.28) reduce to

$$\sin \frac{\alpha_1}{\gamma} = 0, \quad \text{i.e.} \quad \frac{\alpha_1}{\gamma} = n\pi. \quad (4.1)$$

$$\text{From } (3.26) \quad \frac{c^2}{v^2} = 1 - n^2 \pi^2 \gamma^2. \quad (4.2)$$

The group velocity, u , is then given by

$$\frac{c}{u} = c \frac{d(\omega/v)}{d\omega} = \frac{1}{(1 - n^2 \pi^2 \gamma^2)^{1/2}}. \quad (4.3)$$

A formula equivalent to (4.3) was derived by Haubert (1946).

In figure 4, $(c/u - 1)$ is plotted against γ for the fundamental mode, $n = 1$.

The solution fails for $n\pi\gamma > 1$, i.e. $\tau > 2h/cn$,

or taking $h = 75$ km., $n = 1$, $\tau > 0.5$ msec. This solution therefore does not cover the range of periods of the slow components. The periods are those of the oscillatory component and the calculated frequency-group velocity relationship was therefore compared with that observed in daylight atmospherics.

For the comparison a group of six atmospherics occurring at 12.00 hr. on 10 June 1939 was selected. The D.F. distance was 1200 km.

Let t_0 be the time of arrival of the first disturbance from an atmospheric originating at distance s at time $t = 0$, and let t be the time of arrival of a wave of period τ travelling with group velocity u , then

$$\frac{c}{s}(t - t_0) = \frac{c}{u} - 1, \quad (4.4)$$

assuming that the first disturbance travelled with the velocity of light.

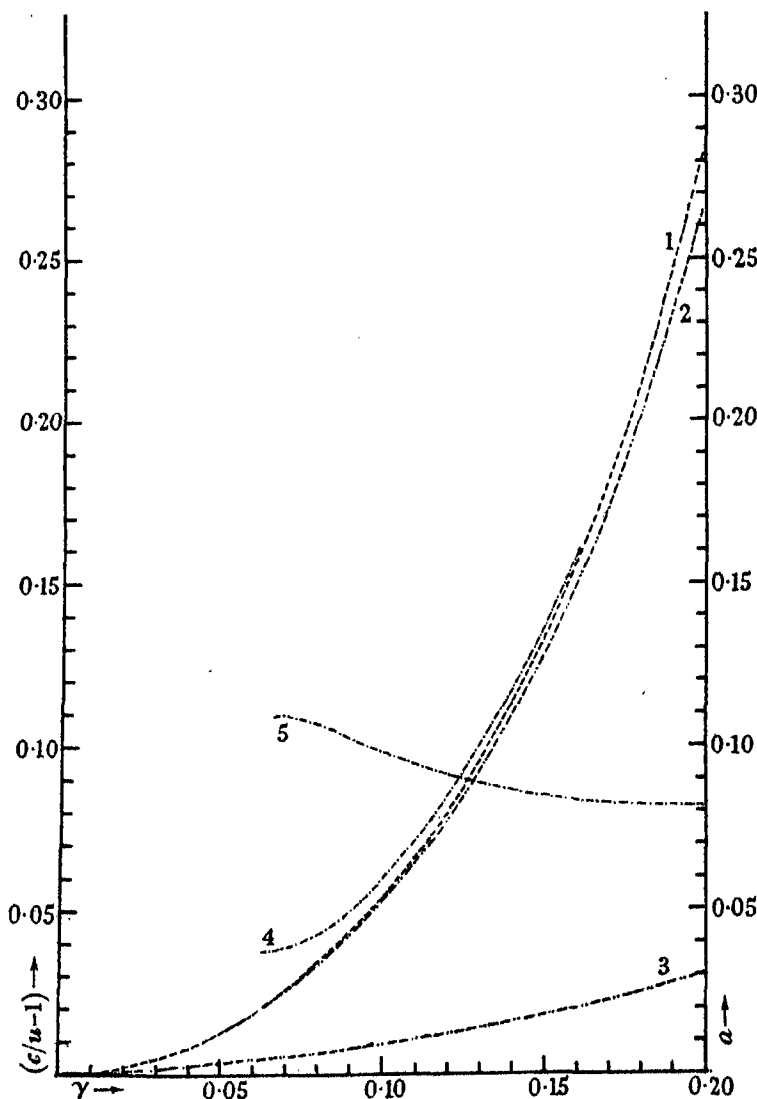


FIGURE 4. Curves of $c/u - 1$ and a against γ . (1) $c/u - 1$, for perfect conductors. (2) $c/u - 1$ horizontal polarization, $k = 0.04$, mode corresponding to (1). (3) a , horizontal polarization, $k = 0.04$, mode corresponding to (1). (4) $c/u - 1$, vertical polarization, $k = 0.04$, mode corresponding to (1). (5) a , vertical polarization, $k = 0.04$, mode corresponding to (1).

Measurements were made of the time interval between the first departure from the central line and each later crossing. Let this interval be t_n . It was assumed that the wave of period $\tau = t_{n+1} - t_{n-1}$ had arrived at time $\bar{t} = \frac{t_{n+1} + t_{n-1}}{2}$ so that $\bar{t}$ represented the quantity $t - t_0$ of equation (4.4), and (4.4) may therefore be rewritten as

$$1 + c\bar{t}/s = c/u. \quad (4.5)$$

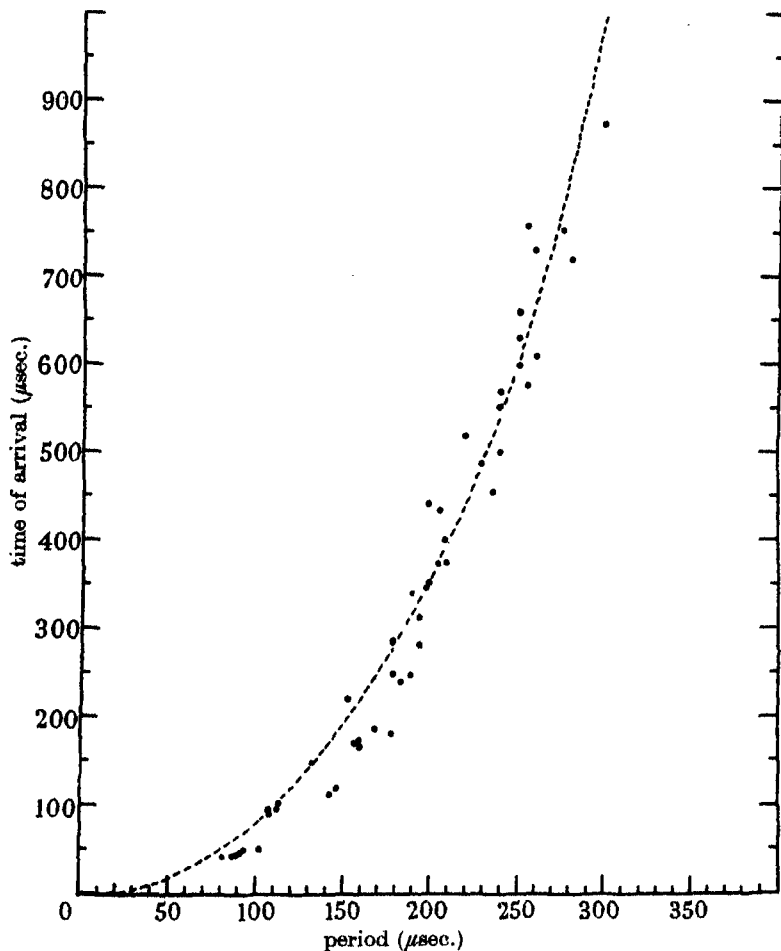


FIGURE 5. Time of arrival against period for six daylight atmospherics.

ct/s was then plotted against τ in figure 5. The curve of that figure is that obtained by calculation from (4.3) and (4.4), taking $s = 1200$ km., $h = 75$ km. The curve fits the observations reasonably well, but it should be remarked that the corresponding curve for $s = 600$, $h = 57.5$ km. fits just as well.

As stated in § 1, Schonland and his associates had found that the spacing of the waves in daylight atmospherics conformed to the Laby formula for reflexions from

an ionospheric layer at a height of about 60 km. This raises the question of the relationship between the two modes of approach.

Consider a record consisting of a series of pulses as shown in figure 6. Laby's formula (the notation has been changed slightly) is

$$\frac{ct_{2n}}{s} = \left(1 + \frac{h}{R} + \frac{16n^2h^2}{s^2}\right)^{\frac{1}{2}} - 1, \quad (4.6)$$

R being the radius of the earth.

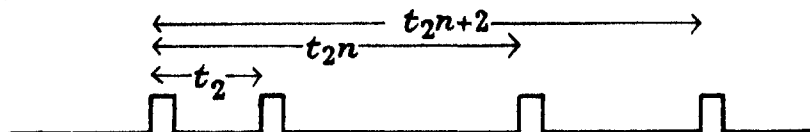


FIGURE 6

Defining $\bar{t}$ and τ as above it can be shown that (4.6) is equivalent to

$$\left(1 + \frac{c\bar{t}}{s}\right)^2 = \frac{1 + (h/R)}{1 - (c^2\tau^2/4h^2)} + \frac{h^2}{s^2} \quad (4.7)$$

or, in terms of γ ,

$$\left(1 + \frac{c\bar{t}}{s}\right)^2 = \frac{1 + (h/R)}{1 - \pi^2\gamma^2} + \frac{h^2}{s^2}. \quad (4.8)$$

Using the formula for group velocity given in (4.3) and (4.4)

$$\left(1 + \frac{c\bar{t}}{s}\right)^2 = \frac{1}{1 - \pi^2\gamma^2}. \quad (4.9)$$

(4.8) and (4.9) differ only by the small quantities h/R (which arises because of the curvature of the earth and was neglected in the present development) and h^2/s^2 . Both these terms are small and it is not practicable to discriminate between (4.8) and (4.9) on the present observations. The discussion has, however, shown that, in the case of perfect conductors, there is no solution corresponding even remotely to the slow component.

5. LAYERS OF FINITE CONDUCTIVITY—SOLUTIONS CORRESPONDING TO THOSE OF § 4

In general $p^2 = \epsilon - \frac{4\pi i\sigma}{\omega}$. It will now be assumed that σ is sufficiently large so that $4\pi\sigma/\omega \gg \epsilon$,

$$p^2 = -\frac{4\pi i\sigma}{\omega} = -\frac{4\pi i\sigma h\gamma}{c},$$

and $1/p^2$ and higher powers may be neglected. With these assumptions (3.27) and (3.28) reduce respectively to

$$\tan \frac{\alpha_1}{\gamma} = -\frac{k(1-i)}{\alpha_1\sqrt{(2\gamma)}}, \quad (5.1)$$

$$\tan \frac{\alpha_1}{\gamma} = -\frac{k\alpha_1(1-i)}{\sqrt{(2\gamma)}}, \quad (5.2)$$

where

$$k = \left(\frac{c}{4\pi h}\right)^{\frac{1}{2}} (\sigma_0^{-\frac{1}{2}} + \sigma_2^{-\frac{1}{2}}). \quad (5.3)$$

Since α and v are now complex it is convenient to write

$$\frac{1}{v} = R\left(\frac{1}{v}\right) + iI\left(\frac{1}{v}\right),$$

so that $\exp\{i\omega(t-x/v)\} = \exp\left\{i\omega\left(t - R\left(\frac{1}{v}\right)\right)\right\} \exp\left(-\frac{ax}{h}\right),$

where $a = -\omega h I\left(\frac{1}{v}\right) = -\frac{1}{\gamma} I\left(\frac{c}{v}\right).$

Solutions of (3.27) and (3.28) corresponding to those already found for perfect conductors can be found numerically, using the perfect conductor solution $R(\alpha) = n\pi\gamma$, $I(\alpha) = 0$ as a starting point. u and a are plotted against γ in figure 4 for $k = 0.04$.

The curves for horizontal polarization do not differ very greatly from those for perfect conductors. For vertical polarization the attenuation is much greater than for horizontal polarization and the curves begin at finite values of γ .

6. LAYERS OF FINITE CONDUCTIVITY—THE SLOW COMPONENT

It has been established that in the case of perfect conductors the only solutions relate to the oscillatory component. The corresponding solutions for finite conductivity were discussed in the preceding section. It remains to be seen whether there is a solution of (5.1) or (5.2) which has no counterpart in the perfect conductor case.

Assuming that α_1/γ is small it is easily found from (5.1) (vertical polarization) that, to a first approximation,

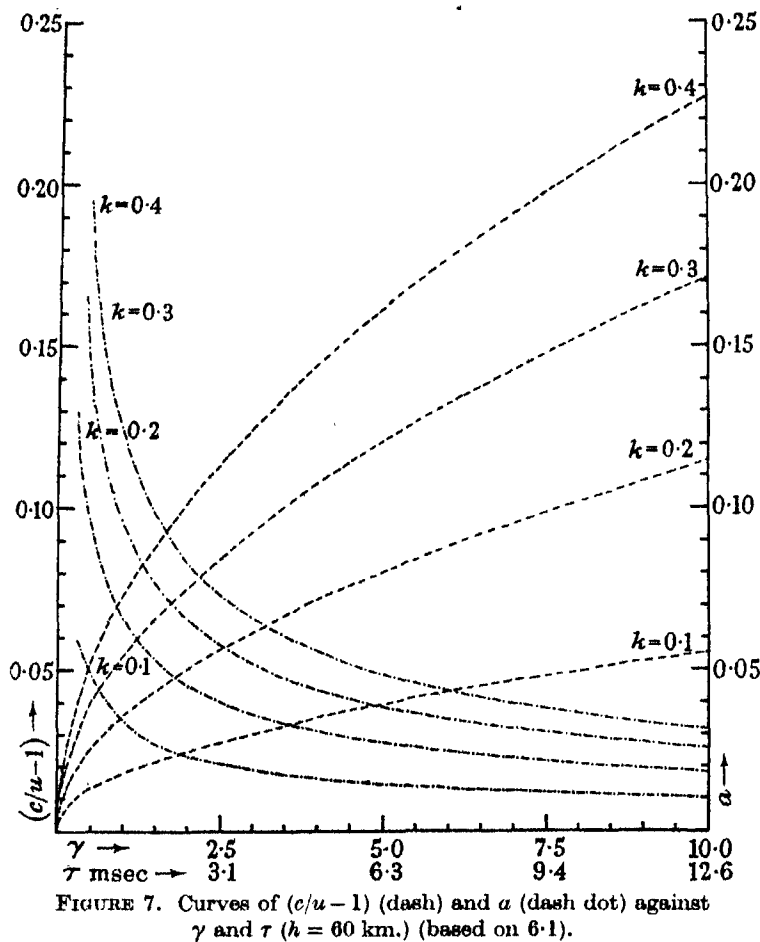
$$\alpha_1 = k^{\frac{1}{2}} \gamma^{\frac{1}{2}} e^{3\pi i/8}. \quad (6.1)$$

There is no corresponding solution of (5.2) (horizontal polarization). Values of u and a calculated from the value of α_1 given in (6.1) are plotted against γ and τ ($h = 60$ km.) in figure 7. The periods are of the right order of magnitude for the slow component.

Watson-Watt *et al.* remark (1937, p. 280) that near the source the slow component starts before the oscillatory component, there being considerable variation in the interval between the starting times. In figure 2 the mean interval is shown as 0.5 msec. and this interval has been used in deriving the velocities of table 1. Since the present discussion is concerned only with the mode of propagation and velocities, the significance of the difference in starting times with respect to the physical conditions governing the development of the slow and oscillatory components at the source will not be discussed here.

The figures in table 1 were derived from figure 2. The table gives (1) the distance, (2) the time interval between the oscillatory and slow components, (3) the value of $c/u - 1$ calculated on the assumption that the first onset of the oscillatory component travelled with velocity c , (4) the quasi period of the slow component, (5) the value of γ calculated from (4) with $h = 60$ km., (6) the values of k found by interpolation, or

extrapolation from the curves of figure 7, (7) the values of σ_2 calculated from (5.3) (σ_0 has been taken as infinite). Where values of k and σ_2 have not been given it is because the values of $c/u - 1$ lie so far outside the range of figure 7 that the extrapolation would be unreliable. It is clear, however, that these points correspond to considerably lower values of σ_2 .



The bias of the observations to larger values of k at short distances is consistent with the proposed mode of propagation since, as k increases, so also does the attenuation, and therefore it is to be expected that points corresponding to large values of k should only be found at limited distances from the source.

The same type of conclusion can be drawn from figure 3. The curves in that figure are drawn for $c/u - 1 = 0.075, 0.125$ and 0.25 with arbitrary zeroes. It will be seen that the most usual value of $c/u - 1$ for the larger distances is in the neighbourhood of 0.125 and that a large proportion of the observations can be included between curves for $c/u - 1 = 0.075$ and 0.25 . Taking $\tau = 10$ msec., corresponding to distances

of 2000 to 5000 km., σ_2 lies between 1.7×10^3 and 18×10^3 e.s.u. Once again a considerable number of points at the shorter distances correspond to larger values of c/u , larger values of k , and smaller values of σ_2 .

TABLE 1

distance (km.)	interval between slow and oscillatory components (msec.)	$c/u - 1$	quasi- period (msec.)	$\gamma = cr/2\pi h$ $h = 60$ km.	k	σ_2 e.s.u. ($\times 10^{-3}$)
200	0.34	0.50	3.8	3.0	—	—
300	0.41	0.41	2.8	2.3	—	—
400	0.69	0.52	3.4	2.7	—	—
500	0.81	0.48	3.2	2.5	—	—
600	0.95	0.47	3.6	2.9	—	—
700	1.09	0.47	5.5	4.4	—	—
800	0.72	0.27	6.8	5.4	0.6	1
900	0.91	0.30	4.1	3.3	—	—
1000	1.41	0.42	7.0	5.6	—	—
1500	1.56	0.31	10.5	8.3	0.6	1
2000	1.60	0.24	7.9	6.3	0.53	1.4
2500	1.60	0.19	8.7	6.9	0.40	2.5
3000	1.78	0.18	11.2	8.9	0.33	3.7
5000	2.01	0.12	9.9	7.9	0.24	6.9

The order of magnitude found for σ_2 is much lower than that given by Appleton (1935) for the ionosphere. This is consistent, as Appleton's discussion referred to layers effective at much higher frequencies than those under discussion here. The values of σ_2 depend on the choice of h . This choice was to some extent arbitrary since the only relevant information is that the reflexion formula applied to daylight atmospherics gives an effective height of 60 km. Any permissible change in h (say to 90 km.) would not, however, affect the order of magnitude for σ_2 .

Another point which may be noted in favour of the proposed explanation is that owing to the rapid increase in the value of a below $\gamma = 1$ there is no question of the higher frequencies of the oscillatory component being propagated in this mode.

Qualitatively therefore the proposed mode of propagation does fit the observed facts.

My thanks are due to Dr B. F. J. Schonland, F.R.S., for suggesting this problem and for much helpful discussion.

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Magnetization curves for ferromagnetic single crystals

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Magnetization curves for iron single crystals above the 'knee' are derived on the basis of domain theory for the case where the specimen is finite and the field is applied in an arbitrary direction with respect to the crystal axes. The shape of the specimen is important for the magnetization process and it is shown that in many cases the demagnetizing field must be such as to make the field actually acting in the crystal have a direction of symmetry (e.g. [111] or [110]) whatever the direction of the applied field. The cases of an oblate spheroid with its equatorial plane a (100) plane of the crystal and of a long rod with arbitrary orientation are considered in detail. In these cases simple expressions for the magnetization curves are obtained. There is good agreement with the experimental results of various authors for both parallel and normal components of magnetization. A method for correcting for the effect of internal strains is indicated.

1. INTRODUCTION*

It is well known that the experimentally observed magnetization curves for ferromagnetic single crystals, where the field is applied along one of the principal directions of the crystal, can be satisfactorily accounted for by the domain theory as developed by Akulov (1931) and others (Becker & Döring 1939, chapter 9). Becker & Döring have, however, pointed out (p. 121) that it is difficult to extend the theory to cover arbitrary directions of the applied field and Takagi (1939) and von Engel & Wills (1947), considering experimental results by Honda & Kaya (1926), have concluded that the simple theory needs modification in order to explain observed facts. The difficulties arise when the direction of magnetization is not the same as that of the applied field, since in this case, the demagnetizing field—inevitable in a finite crystal—may modify not only the magnitude but also the direction of the field actually acting in the interior of the crystal, and the problem of finding the equilibrium configuration of domains is at first sight very complicated. The present investigation nevertheless shows that for the shapes of specimen of greatest practical interest, a strict application of simple domain theory leads to reasonably simple results which agree well with experiment. By a suitable averaging process, the magnetization curves for single crystals with different orientations can be combined to give curves for polycrystalline specimens, but this development will not be dealt with in this paper.

2. PRINCIPLES OF DOMAIN THEORY FOR IRON CRYSTALS

According to domain theory the intensity of magnetization in a ferromagnetic is everywhere equal to the saturation intensity I_s but the direction of the magnetization varies from place to place in such a way as to make the free energy of the system

* After this paper was completed, a paper by Néel (1944), dealing with the same subject, was brought to our notice. It is hoped that the present paper may still be of interest as its treatment differs from Néel's in various ways. A summary of Néel's paper in relation to the present one is given in the Appendix.

a minimum. A region in which the magnetization is constant in magnitude and direction is called a domain. The free energy is the sum of three terms, crystal energy, magnetic potential energy and strain energy; the last of these is zero in an ideal crystal and the other two are given, per unit volume, by the expressions

$$E_K = K_1(\omega_1^2\omega_2^2 + \omega_2^2\omega_3^2 + \omega_3^2\omega_1^2) + K_2\omega_1^2\omega_2^2\omega_3^2,$$

the first two terms of the power series in the ω 's for a cubic crystal, and

$$E_H = -I_s H \cos \chi$$

respectively, where K_1 and K_2 are 'anisotropy constants', $\omega_1, \omega_2, \omega_3$, the direction cosines of the magnetization with respect to the crystal axes, H the magnetic field and χ the angle between H and I_s . When K_1 is positive, as in iron, it follows that in zero field the six cube edge directions ([100] directions)* are directions of minimum energy of magnetization. As soon as a small field is applied, the [100] direction nearest to the field provides the deepest energy minimum and the domain magnetization will take up this direction. If the field is increased, the magnetization will turn from the [100] direction towards the field so as to keep the free energy a minimum, and this turning will increase the component of magnetization in the field direction. The free energy is

$$E = -I_s H \cos \chi + K_1(\omega_1^2\omega_2^2 + \omega_2^2\omega_3^2 + \omega_3^2\omega_1^2) + K_2\omega_1^2\omega_2^2\omega_3^2 \quad (1)$$

per unit volume and from the condition that this should be a minimum, the following relations giving the magnetization when a field H is applied along the principal directions of the crystal are obtained (Akulov 1929, 1931; Gans & Czerlinski 1932):

$$\text{If } \frac{I}{I_s} = \eta$$

$$H \text{ along } [100] \quad \eta = 1 \quad \text{for all } H > 0, \quad (2)$$

$$H \text{ along } [110] \quad \eta^3 - \frac{1}{2}\eta = \frac{HI_s}{4K_1}, \quad (3)$$

$$H \text{ along } [111] \quad \frac{K_1}{3}\{\eta(7\eta^2 - 3) + \sqrt{2}\sqrt{(1 - \eta^2)(4\eta^2 - 1)}\} + \frac{K_2}{18}\{\eta(1 - 16\eta^2 + 23\eta^4) - \sqrt{2}\sqrt{(1 - \eta^2)(1 - 9\eta^2 + 10\eta^4)}\} = HI_s. \quad (4)$$

In these three simple cases the magnetization is in the same direction as the applied field and the calculations agree well with experiment. In other cases, as already pointed out, the calculation is complicated by demagnetizing effects which depend on the shape of the specimen. We shall consider two shapes only, that of an oblate spheroid and that of a long rod. These are the shapes for which most experimental data are available.

* In the text of this paper, [100] is taken to represent any one cube edge, not a particular one. In other words, no attempt has been made to name each cube edge separately, e.g. [010], [001], etc. The same applies to [110] and [111]. In the diagrams for clarity, the separate directions have, however, been specified in the usual manner.

The case of the oblate spheroid where the equatorial plane is a (100) plane of the crystal and the magnetic field is applied in this plane is particularly simple since the problem becomes a two-dimensional one. This orientation for the oblate spheroid will be considered first and is the only one that will be dealt with in detail.

3. OBLATE SPHEROID

Let the demagnetizing coefficient (the same for all directions in the plane of the spheroid) be N . Then if I is the mean magnetization of the crystal, the contribution of magnetic potential energy to the free energy of the crystal is given not simply by $-\mathbf{I} \cdot \mathbf{H}_e$, the potential energy per unit volume of $\mathbf{I}$ in the applied field $\mathbf{H}_e$, but by $-\mathbf{I} \cdot \mathbf{H}_e + \frac{1}{2}NI^2$, the extra term representing the energy in the demagnetizing field. This additional term in the free energy may considerably affect the process of magnetization. In a system with no self-demagnetization the free energy, given by (1), is a minimum when the domain magnetization I_s has the same direction at all points; when the term $\frac{1}{2}NI^2$ is added to (1), the minimum of E may be achieved by an arrangement which splits the material into domains having different directions of I_s so that I is reduced and $\frac{1}{2}NI^2$ decreases by more than the other energy terms increase. In writing the demagnetization energy as $\frac{1}{2}NI^2$ it is assumed that the demagnetizing field $-NI$ is uniform throughout the crystal. This assumption is justified if the domains into which the crystal is divided are small compared with the crystal dimensions and if there are no 'free poles' of I in the body of the crystal. The small size of domains is shown by many experiments and it can be shown that the presence of any appreciable density of 'free poles' would lead to energy densities far higher than those involved in the arrangements we shall consider.

It can be seen, by considering the effect of a change in the direction of magnetization of a small region of the crystal,* that E can be a minimum only if at every point in the material the direction of I_s is such as to make the energy given by (1) a minimum, where $\mathbf{H}$ is taken to be the resultant field in the crystal, the vector sum of the

* If a small fraction of the crystal has its magnetization (I_s) at an angle α to the mean magnetization, I_1 , of the rest of the crystal, then

$$\frac{1}{2}NI^2 = \frac{1}{2}N((1-f)^2 I_1^2 + 2(1-f) I_1 \cdot f I_s \cos \alpha)$$

and the rate of change of free energy per unit volume of the whole crystal when the fraction f changes its direction of magnetization, the magnetization of the rest of the crystal remaining constant, is

$$\frac{1}{f} \frac{dE}{d\alpha} = \frac{dE_K}{d\alpha} - I_s H_e \frac{d}{d\alpha} (\cos \chi) + NI \cdot I_s \frac{d}{d\alpha} (\cos \alpha),$$

neglecting quantities of the order of $fI_s/(1-f) I_1$ in comparison with unity. The crystal can only be in equilibrium if $dE/d\alpha = 0$ for all possible changes. The equation shows that this condition is the same as the condition that the energy given by (1) should be a minimum for every part of the crystal, where the field H of (1) is taken to be the resultant field, the vector sum of H_e and the demagnetizing field $-NI$.

It has been assumed that the change in α has been made without creating any 'free poles' of I in the crystal. More detailed consideration shows that it is always possible to make such a change.

applied field H_e and the demagnetizing field $-NI$. We can therefore say that the whole crystal can be in a state of minimum energy only when each of its domains is in a state of minimum energy, calculated as the sum of crystal energy and energy in the resultant field. When H is zero there are four directions of minimum energy, the zeros of crystal energy (in the (100) plane), and the magnetization in each domain may have any of these directions. The effect of a field H is to change the positions of these minima and to make some deeper than others. Since wall movements between domains with different directions of magnetization are supposed to be able to occur freely, the equilibrium state, giving minimum free energy for the whole crystal, will be one where all domain magnetizations have the direction of the deepest energy minimum. If, however, all domains are magnetized in the same direction then the demagnetizing field will be $-NI_s$ in the opposite direction and for small values of H_e the resultant field will have such a direction that the deepest energy minimum is not the one in whose direction the domains are magnetized, and consequently the arrangement is not one of minimum energy. This is the case foreseen above when the energy term $\frac{1}{2}NI^2$ leads to a minimum energy configuration in which the direction of magnetization is not the same at all points. The only arrangement where the energy of the crystal can be a minimum with different domains magnetized in different directions is one where there are two or more 'deepest minima' of energy for the domains. This can happen when the resultant field is zero, giving four equal minima or when it has a direction symmetrically between two of the minima of the crystal energy, i.e. a [110] direction, giving two equal minima.

We can say that in the region of small H_e any arrangement where all domains have one particular direction of magnetization is unstable because the demagnetizing field is such as to make some other of the directions of minimum energy more favourable. The only stable arrangement is one where domains are distributed between more than one energy minimum and such a distribution is only possible if the resultant field $H_e - NI$ is symmetrical between two or more crystal energy minima. This condition of symmetry for H determines the distribution of domains between the energy minima since the mean magnetization I , and hence $-NI$ which determines the direction of H , depends on this distribution. As will be seen later, the distribution of domains between energy minima must change as H_e changes in order to preserve the symmetry of H ; as H_e increases the number of domains in the minimum whose direction is nearest to that of H_e will increase while the numbers in other minima decrease. Any distribution other than that required to make H symmetrical will be one for which the free energy of the crystal is not a minimum, since changes in the direction of magnetization of some part of the crystal would decrease the energy.

The first part of the magnetization process is the turning of domain magnetizations from one [100] direction to another, a process which occurs for infinitesimal values of H ; this is the region of symmetry given by $H = 0$ with four possible directions of magnetization. The components of the magnetization, I_p parallel to H_e and I_n ,

perpendicular to it can be deduced very simply, for, since $H = 0$, its components $H_e - NI_p$ and NI_n must each be equal to zero giving

$$I_p = \frac{H_e}{N}, \quad (5)$$

and

$$I_n = 0. \quad (6)$$

As H_e is increased, therefore, I_p will increase through the turning of domains from other [100] directions into the two [100] directions nearest to H_e , but the distribution of domains between these two will always be such that $I_n = 0$. This process will be complete when all the domains are distributed between the two directions. If H_e is increased further, there is no possible arrangement of domains among [100] directions that can make $H = 0$, so that H will have a finite value and, as discussed above, its direction must lie symmetrically between two [100] directions (i.e. in a [110] direction). When H has a finite value the energy minima are, by equation (1), turned from the [100] directions towards the direction of H and the magnetization is thus increased. It can be seen that as H_e is increased, the distribution of domains between the minima that is required to make H have a [110] direction will change, the proportion of domains in the direction nearer to H_e increasing. In this region, which we shall call the 'two-vector' region, we can calculate the magnetization as follows.

The field H has a direction symmetrically between two [100] directions, i.e. a [110] direction of the crystal. The magnitude of the component of magnetization in this direction will be independent of the distribution of domains between the [100] directions; it is in fact the same as the magnetization $I_{[110]}(H)$ that would be produced by a field H applied to an infinite crystal in a [110] direction, and is given by equation (3). We can therefore derive the value of the field H as the sum of the component of H_e in the [110] direction and the component of the demagnetizing field in the same direction,

$$H = H_e \cos(45^\circ - \lambda) - NI_{[110]}(H),$$

where λ is the angle between H_e and the nearest [100] direction, giving

$$H_e = \sec(45^\circ - \lambda) \{H + NI_{[110]}(H)\}. \quad (7)$$

Knowing H_e in terms of H , we can calculate I_p and I_n from the condition that the demagnetizing field must make H lie in a [110] direction:

$$H \cos(45^\circ - \lambda) = H_e - NI_p,$$

$$H \sin(45^\circ - \lambda) = NI_n,$$

giving

$$I_p = \frac{H_e - H \cos(45^\circ - \lambda)}{N}, \quad (8)$$

$$I_n = \frac{H}{N} \sin(45^\circ - \lambda). \quad (9)$$

Equations (7), (8) and (9), together with equation (3) giving $I_{[110]}(H)$, determine the magnetization. Figure 1 shows the values of I_p and I_n calculated in this way for

$\lambda = 20^\circ$, $N = 0.184$, $K_1 = 4.2 \times 10^5 \text{ erg./cm.}^3$, conditions corresponding to an experiment by Honda & Kaya (1926), whose experimental results are also shown in the figure. The parts Ox of the curves correspond to equations (5) and (6) for the region where $H = 0$, the parts xy to equations (7), (8) and (9). The 'knee', x , between the two regions occurs where $H = 0$ in equations (7), (8) and (9), giving

$$I_n = 0, \quad I_p = \frac{H_c}{N} = \frac{I_s}{\cos \lambda + \sin \lambda}. \quad (10)$$

Equations (7), (8) and (9) apply so long as H remains in the $[110]$ direction but, as was seen above, this condition becomes unnecessary for large values of H_c (depending on N and λ) because a stable arrangement with all domains in one direction, a 'single-vector' arrangement, becomes possible. For this region we can calculate the magnetization as follows (Honda & Okubo 1916).

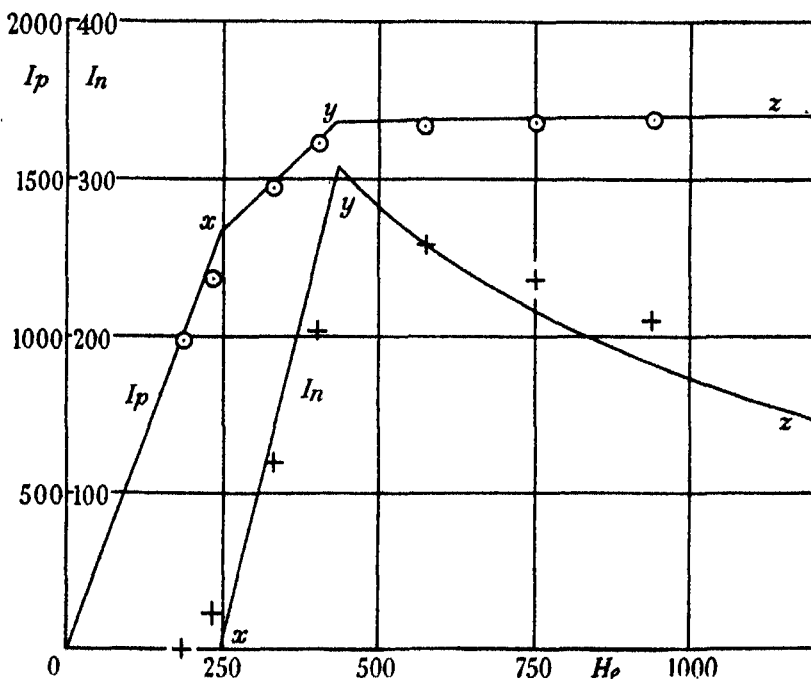


FIGURE 1. Calculated magnetization curves for oblate spheroid, with $\lambda = 20^\circ$. Experimental points from Honda & Kaya (1926). Magnetization I_p , I_n , in gauss, applied field, H_e , in oersteds.

We will suppose that the domains, all lying in the same energy minimum, have turned through an angle β from the $[100]$ direction. The free energy of the domains will be

$$E = E_K(\beta) - I_s H_e \cos(\lambda - \beta) + \frac{1}{2} N I_s^2,$$

and the condition for equilibrium is

$$\frac{dE}{d\beta} = \frac{d}{d\beta} E_K(\beta) - I_s H_e \sin(\lambda - \beta) = 0, \quad (11)$$

where $E_K(\beta)$ is the crystal energy which, in this case, simplifies to

$$E_K(\beta) = K_1 \sin^2 \beta \cos^2 \beta.$$

Thus

$$\frac{d}{d\beta} E_K(\beta) = \frac{K_1}{2} \sin 4\beta,$$

so that we have

$$H_c = \frac{K_1}{2I_s} \frac{\sin 4\beta}{\sin(\lambda - \beta)}. \quad (12)$$

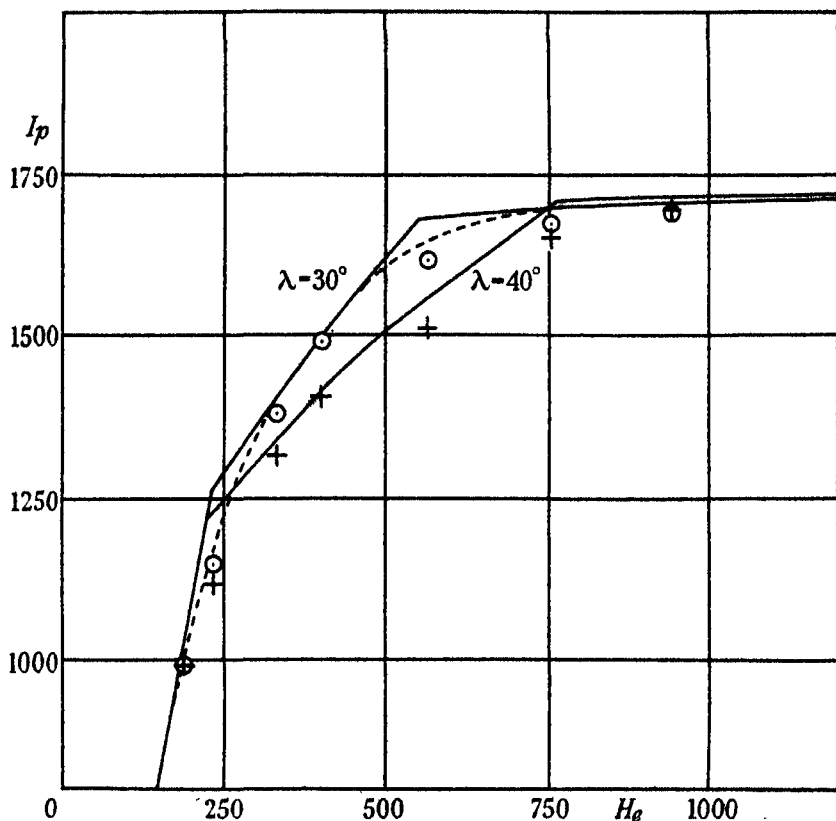


FIGURE 2. Calculated magnetization curves for oblate spheroid with $\lambda = 30^\circ$ and $\lambda = 40^\circ$. Experimental points from Honda & Kaya (1926). Parallel component of magnetization, I_p , in gauss, applied field, H_c , in oersteds.

$$I_p \text{ and } I_n \text{ are given by} \quad I_p = I_s \cos(\lambda - \beta), \quad (13)$$

$$I_n = I_s \sin(\lambda - \beta). \quad (14)$$

Equations (12), (13) and (14) determine the magnetization for the 'single-vector' region, and give the sections $y-z$ of figure 1. The intersection y between the curves for the 'two-vector' and the 'single-vector' regions clearly determines the point at which $\mathbf{H}$ just leaves the $[110]$ direction, and all domains lie in one direction rather than distributed between two. It can be verified by more detailed calculation that

the number of domains in one direction tends to zero as we approach y along the 'two-vector' curve and the direction of $\mathbf{H}$ tends to $[110]$ as we approach y along the 'single-vector' curve, as would be expected.

Magnetization curves calculated in the same way for $\lambda = 30^\circ$ and $\lambda = 40^\circ$, using the same values for N and K_1 , are shown in figures 2 and 3 together with the experimental points obtained by Honda & Kaya. In all cases it will be seen that the agreement with experiment is quite good; in fact, bearing in mind uncertainties in

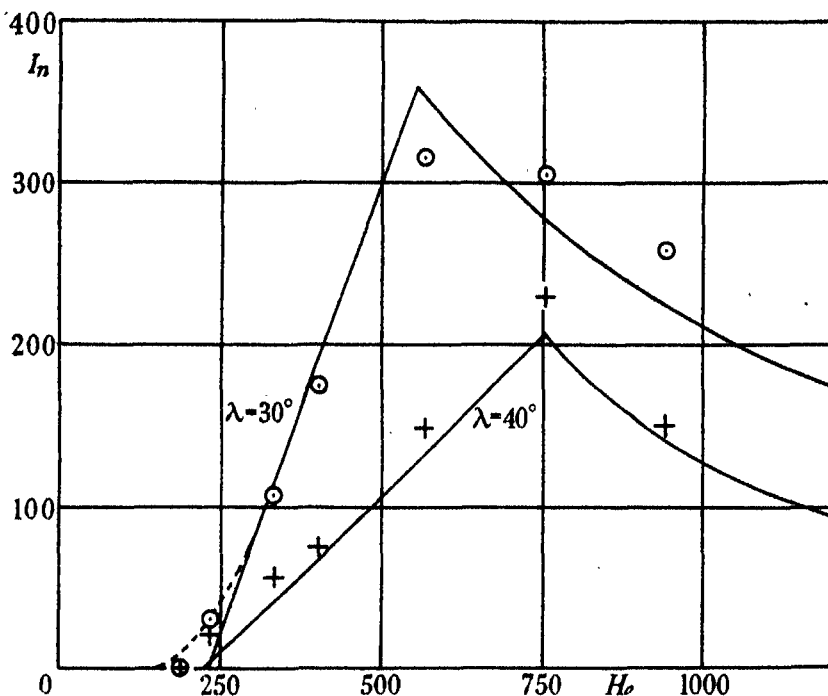


FIGURE 3. Calculated magnetization curves for oblate spheroid with $\lambda = 30^\circ$ and $\lambda = 40^\circ$. Experimental points from Honda & Kaya (1926). Normal component of magnetization, I_n , in gauss, applied field, H_a , in oersteds.

the experimental results, such as rotational hysteresis and corrections for air flux, and possible errors in the value of N and K_1 , it may be said that there is no significant difference between theory and experiment. The experimental I_p curves are a little lower and more rounded than the theoretical ones; similar differences are well known to exist between experimental and theoretical curves for magnetization in the principal directions of the crystal (Becker & Döring 1939, p. 118) and are usually attributed to internal strains. Gans & Czerlinski (1932) have proposed a method for correcting curves for strain energy by use of the experimental curves for magnetization in a $[100]$ direction, but the validity of their method seems doubtful. With our method of calculation, allowance can be made for strains by using experimental curves obtained in the $[110]$ direction instead of the theoretical equation (3) to give $I_{[110]}(H)$. Using Honda & Kaya's results for $I_{[110]}(H)$, the curves of figures 1, 2 and 3,

are modified slightly and agree rather better with experimental values as shown by the dotted lines of figures 2 and 3. (Curves corrected in this way are shown for $\lambda = 30^\circ$ only.)

The upper part of the I_n curves ($y-z$ in figure 1) have been obtained before and are known to agree with experiment for large H_e , i.e. at points well to the right of figure 1 (Honda & Okubo 1916; Webster 1925; Gans 1933).

The observed values of I_n to the left of the transition point y , do not appear to have been explained previously* without modification of the simple domain theory. Takagi (1939) and von Engel & Wills (1947) developed a statistical theory in order to explain the curves; the theories involved the introduction of an arbitrary energy parameter E_0 which had to be found by comparison with experiment; E_0 was found to be much larger than the thermal energy and no satisfactory interpretation of E_0 has been given. It now appears that the I_n curves can be explained by a strict application of the simple form of the domain theory, good agreement with experiment being obtained using only values of constants that are already determined by independent experiments.

A further check of the main idea of our theory can be made by determining the direction of H in the experiments of Honda & Kaya. The theory predicts that for external fields H_e up to several hundred gauss the resultant field H should lie in a $[110]$ direction. The resultant field can be calculated from the experimental values of H_e , I_p , I_n and N and is in fact found to lie close to a $[110]$ direction in the appropriate range of H_e . The test is not very exact since the direction of H is sensitive to errors in the experimental data for I_p and N . The fact that H is frequently found to lie near a $[110]$ direction was commented on by von Engel & Wills (p. 481) but was found to conflict with, rather than to support, their theory.

4. LONG ROD

The other shape of specimen we shall consider is a long rod with the external field applied in the direction of its length. The rod is taken to be so long that there is no demagnetizing effect along its length, while the demagnetizing coefficient in all directions at right angles is of the order of 2π . The orientation of the rod will be defined by $\alpha_1, \alpha_2, \alpha_3$, the direction cosines of its axis with respect to the crystal axes.

It will be shown that it is possible to calculate the component of magnetization parallel to the rod (I_p) to a very close approximation without knowing the exact value of the demagnetizing coefficients N perpendicular to the rod. It is not possible to calculate the normal component of magnetization I_n without knowing N , but the value of I_n is always small and no measurements of I_n for long rods appear to have been made, so our calculations will be confined to I_p .

As before, the first part of the magnetization process is the turning of domains into the easy directions nearest to the field,* and will be completed in an infinitesimal field H , which in this case corresponds to an infinitesimal external field H_e , since

* But see footnote, p. 72.

there is no demagnetization in the direction of H_e . The distribution of domains when this process is complete, must however, be such as to make I_n zero since a finite I_n would produce a finite demagnetizing field NI_n perpendicular to the rod and lead to instability of domain distribution of the type discussed in the oblate spheroid case. It can be shown (Becker & Döring, 1939, p. 119) that such a distribution—every domain in one or other of the three directions nearest the field, yet giving $I_n = 0$ —produces a parallel component of magnetization

$$I_p = \frac{I_s}{\alpha_1 + \alpha_2 + \alpha_3}, \quad (15)$$

and this is, therefore, the value of I when the processes occurring in infinitesimal fields are complete. The first part of the magnetization curve (Ox , figure 4) is thus a vertical rise in zero field to the value $I_s/\alpha_1 + \alpha_2 + \alpha_3$. Figure 4 is calculated for an iron single crystal rod (no. 3) measured by Sizoo (1929).

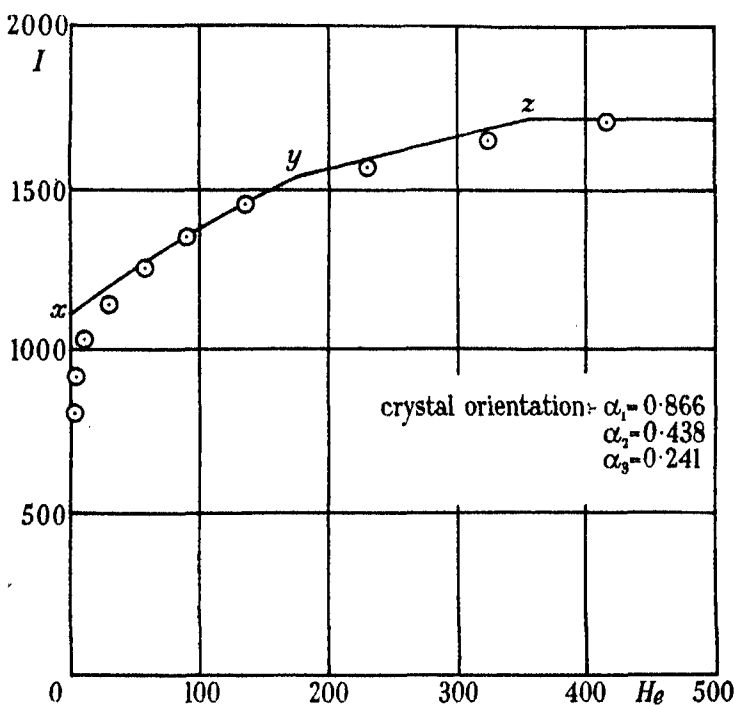


FIGURE 4. Calculated magnetization curve for long rod with orientation corresponding to Sizoo's crystal 3 (1929), for which the experimental values, corrected for longitudinal demagnetizing coefficient ($N = 0.00344$), are shown as $\odot$. Magnetization, I , in gauss, applied field, H_e , in oersteds.

When H_e is increased from its infinitesimal value, H will also increase to a finite value and the same sort of argument as was used in the case of the oblate spheroid shows that, in general, the distribution of domains among the three easy directions nearest to H_e must be such as to make H have a $[111]$ direction, symmetrically

Using this value of H , we can find the intensity of magnetization $I_{[111]}(H)$ in the $[111]$ direction by using equation (4). The component of I in this direction will be correctly given by equation (4) whatever the distribution of domains among the three possible directions, but the distribution may, in fact, be such that I has a considerable component in some other direction. The exact distribution required to make H have a $[111]$ direction cannot be found without knowing the value of N but, as will be shown later, in most cases the direction of I required to produce the necessary demagnetizing field is extremely close to the axis of the rod (the H_e direction). We can therefore find I_p to a close approximation, by assuming that the total magnetization, I , has the direction $(\alpha_1, \alpha_2, \alpha_3)$, while we know that its component in the $[111]$ direction is $I_{[111]}(H)$.

This gives
$$I_p = I = \frac{I_{[111]}(H)}{\cos \psi} = \frac{\sqrt{3} I_{[111]}(H)}{\alpha_1 + \alpha_2 + \alpha_3}. \quad (17)$$

Equations (16) and (17), together with equation (4) for $I_{[111]}(H)$, give the relation between I_p and H_e ; this is the portion x — y of figure 4. For the calculation we have taken $K_2 = \frac{1}{2}K_1$ which is true to the accuracy with which K_2 is known for pure iron and for 3.85 % silicon iron (Becker & Döring 1939, p. 123; Williams 1937).

At this stage we must consider the error caused by assuming that I had the direction of the rod. Actually I will be inclined at a small angle ϵ such that the demagnetizing field $NI \sin \epsilon$, compounded with the field H_e , produces a resultant (H) in the $[111]$ direction. We have, therefore,

$$\frac{NI \sin \epsilon}{H_e} = \tan \psi, \quad (18)$$

and for the specimen of figure 4, taking $N = 2\pi$, $I = 1500$, $H = 160$, $\psi = 26.75^\circ$ we get $\epsilon \sim \frac{1}{2}^\circ$. The fractional error in I_p caused by assuming I to have the direction of the rod is $\{\sec \psi - \sec(\psi - \epsilon)\}/\sec \psi$ which, in this case, is about $\frac{1}{2}\%$ and may be neglected. The error is of the same order of magnitude in most of the other cases considered.

The 'three-vector' region just considered will not extend to saturation, for as the domains turn towards the $[111]$ direction in increasing field, a stage is reached when two of the domain directions (A' and B' in figure 5) become coplanar with H_e . At this stage, even if all domains are distributed between the A' and B' directions only, there will be no demagnetizing field perpendicular to the $DA'H_eB'E$ plane which would cause instability by making the C' direction more favourable than the A' and B' directions. In fields higher than that required to make the A' and B' directions coplanar with H_e , we have therefore a 'two-vector' region, the domains being distributed between two directions A' and B' only, which move towards each other in the DH_eE plane as H_e is increased. H need no longer be symmetrically placed between the three vectors A , B and C , but only between the two, A' and B' , so that it is not confined to the $[111]$ direction but only to the (110) plane (CF in figure 5).

The transition from the 'three-vector' to the 'two-vector' region will, in fact, occur just *before* the domain directions A' and B' become coplanar with H_e because

a 'two-vector' arrangement will be stable even when there is a demagnetizing field perpendicular to the $DH_c E$ plane, provided that this field is insufficient to make the resultant field H lie nearer to C' than to A' or B' . The actual positions of the energy minima at the transition will therefore be at a small angle below the line $DH_c E$ in figure 5, but it can be seen that this angle is of the same order as the angle ϵ of equation (18), and the error in the subsequent calculations, if we assume the angle to be zero, will be negligibly small. At the transition point, H will be in the [111] direction and as H_c increases, the domain magnetizations will move towards the point F in figure 5, remaining just below the line $DH_c E$, but approaching it more and more closely, while H will move down from [111] towards F , remaining in the (110) plane, CF .

With this approximation, that the domain magnetizations are accurately in the plane $DH_c E$ instead of just below it, we can calculate the 'two-vector' part of the magnetization curve (y — z in figure 4). We have first to calculate the angle ϕ between the (110) plane (point F) and the directions of minimum energy A'' or B'' in a given field H_c , then to calculate the distribution of domains between the symmetrical energy minima A'' and B'' and hence find I_T .

Let θ be the angle between the plane $DH_c E$, which contains H_c and is symmetrical with respect to the [100] directions A and B and the (100) plane $DABE$. Let μ be the angle between H_c and the (110) plane CF which lies between A and B . For a given specimen these angles θ and μ (see figure 5) are determined by the orientation ($\alpha_1, \alpha_2, \alpha_3$) according to the equations

$$\sin \theta = \alpha_3 \sqrt{\left(\frac{2}{2 - (\alpha_1 - \alpha_2)^2} \right)}, \quad (19)$$

$$\cos \mu = (\alpha_1 + \alpha_2) \frac{\cos \theta}{\sqrt{2}} + \alpha_3 \sin \theta. \quad (20)$$

In equation (1) for the free energy, when the magnetization is in direction A'' or B'' , χ is the angle between H and direction A'' or B'' and $\omega_1, \omega_2, \omega_3$ are the direction cosines of A'' or B'' given in terms of θ and ϕ by

$$\sqrt{2} \omega_1 = \cos \theta \cos \phi \pm \sin \phi,$$

$$\sqrt{2} \omega_2 = \cos \theta \cos \phi \mp \sin \phi,$$

$$\omega_3 = \sin \theta \cos \phi.$$

Since H_c is the component of H in the direction (θ, μ) so that $H \cos \mu \cos \gamma = H_c$, and it can be seen from figure 5 that

$$\cos \chi = \cos \phi \cos \gamma$$

where γ is the angle between H and the $DH_c E$ plane, we have

$$H \cos \chi = \frac{H_c \cos \phi}{\cos \mu}.$$

The equation for the equilibrium domain direction therefore becomes

$$\left(\frac{\partial E}{\partial \phi}\right)_\theta = 0 = \frac{I_s H_e \sin \phi}{\cos \mu} + \frac{K_1}{2} \sin 2\phi \{\sin^2 \phi (1 + \cos^2 \theta) - 2 \sin^2 \theta + \cos^2 \phi (4 \sin^4 \theta - \cos^2 \theta - \cos^4 \theta)\} - \frac{K_2}{4} \sin^2 \theta \sin 2\phi \{\cos^2 \phi (1 + \cos^2 \theta) - 1\} \{3 \cos^2 \phi (1 + \cos^2 \theta) - 1\}. \quad (21)$$

This equation enables $I_s H_e / K_1 \cos \mu$ to be calculated as a function of θ and ϕ and the numerical results for various values of θ and ϕ are given in table 1. The calculations have been simplified by assuming $K_2 = \frac{1}{2} K_1$ (see above). Values calculated with $K_1 = 0$ are also given in the table and it can be seen that the results depend appreciably on the value of K_2 so that the uncertainties in K_2 will cause some uncertainty in the calculated curves.

TABLE 1. VALUES OF $I_s H_e / (K_1 \cos \mu)$ IN TERMS OF θ AND ϕ , TAKING $K_2 = \frac{1}{2} K_1$, AND (FIGURES IN BRACKETS) $K_2 = 0$

	$\phi = 0^\circ$	10°	20°	30°	40°
$\theta = 0^\circ$	2.00 (2.00)	1.85 (1.85)	1.44 (1.44)	0.87 (0.87)	0.27 (0.27)
10°	2.00 (1.97)	1.85 (1.82)	1.44 (1.42)	0.88 (0.87)	0.28 (0.28)
20°	1.97 (1.84)	1.82 (1.71)	1.42 (1.34)	0.88 (0.82)	—
30°	1.76 (1.56)	1.63 (1.46)	1.28 (1.16)	—	—
$35^\circ 16'$	1.55 (1.33)	—	—	—	—

For a given ϕ the component of I in direction F will be $I_s \cos \phi$, whatever the distribution of domains between A'' and B'' . As before, we can say that the direction of I will be very close to the axis of the specimen so that we have as a good approximation for I_p

$$I_p = I = \frac{I_s \cos \phi}{\cos \mu}. \quad (22)$$

θ and μ are fixed by the orientation of the specimen (equations (19) and (20)) so that for a given specimen the values of I_p and H_e corresponding to a set of values of ϕ can be obtained from equation (22) and table 1 (using graphical interpolation where necessary). This method gives the relation between I_p and H_e plotted as section y — z of figure 4.

This curve for the 'two-vector' region intersects that for the 'three-vector' region in point y . It can be verified by more detailed calculation that the number of domains in the C' direction diminishes to zero as we approach y along the 'three-vector' curve and that the direction of H approaches $[111]$ as we approach y along the 'two-vector' curve, indicating that the intersection at y does genuinely define

the transition from the 'three-vector' to the 'two-vector' region, to the accuracy of the approximation discussed above.

The 'two-vector' region will not extend to saturation for as the domain directions turn towards each other along DH_cE the A'' domains will approach the direction of the specimen axis (H_c) and a point will be reached at which the demagnetizing field, even if all domains have the A'' direction, will be insufficient to make H lie nearer to B'' than to A'' , so that a 'single-vector' arrangement of domains becomes possible without instability. This second transition point is defined by

$$\frac{NI_s \sin(\phi - \mu)}{H_c} = \tan \mu, \quad (23)$$

and therefore depends on the value of N , but in most cases this transition occurs at values of I_p very near saturation, so that a single-vector region is unimportant in magnetization curves as usually plotted. For the specimen of figure 4, for example, the value of I_p at the second transition is $0.997I_s$ if we assume $N = 2\pi$.

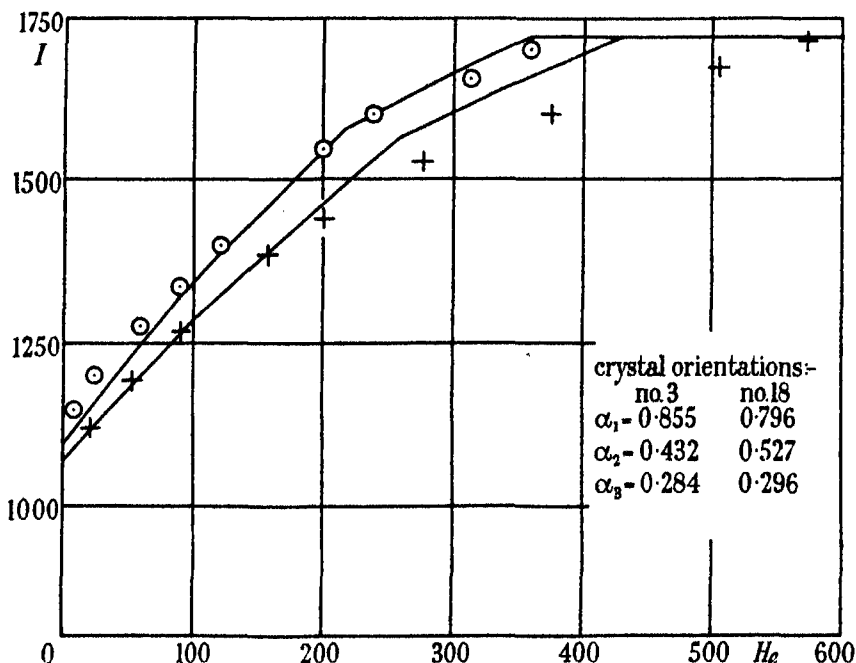


FIGURE 6. Calculated magnetization curves for long rods (iron) with orientations corresponding to Kaya's (1933) crystals 3 and 18. Points taken from Kaya's experimental curves are also shown. Magnetization, I , in gauss, applied field, H_c , in oersteds.

The calculation of the magnetization curve in the 'single-vector' region is a rather complicated three-dimensional problem, since there are no restrictions of symmetry on the direction of H . Becker & Döring (1939) have given a treatment of this last part of the curve which applies, however, only to fields so high that demagnetizing effects can be ignored.

Theoretical $I_p: H_e$ curves calculated by the above methods for various crystals are shown in figures 4, 6 and 7, together with points found experimentally. Figures 4 and 6 refer to crystals of iron used by Sizoo (1929) and Kaya (1933) respectively. The values used for the theoretical curves were $K_1 = 4.2 \times 10^5$ erg/c.c., $K_2 = \frac{1}{2}K_1$, $I_s = 1720$ gauss. Figure 7 refers to two single crystal specimens of 3.15 % silicon-iron about $3 \times 0.1 \times 0.03$ cm.³ for which we ourselves have measured magnetization curves, using a solenoid to provide the field H_e and a small search coil and ballistic galvanometer to measure I . The values used in the calculations were $K_1 = 2.8 \times 10^5$ erg/c.c., $K_2 = \frac{1}{2}K_1$, $I_s = 1605$ gauss. The orientations of all specimens in terms of $(\alpha_1, \alpha_2, \alpha_3)$, are shown in the figures. The orientations of our specimens were found by the method of optical reflexions from etch pits giving an accuracy of 2 to 3°.

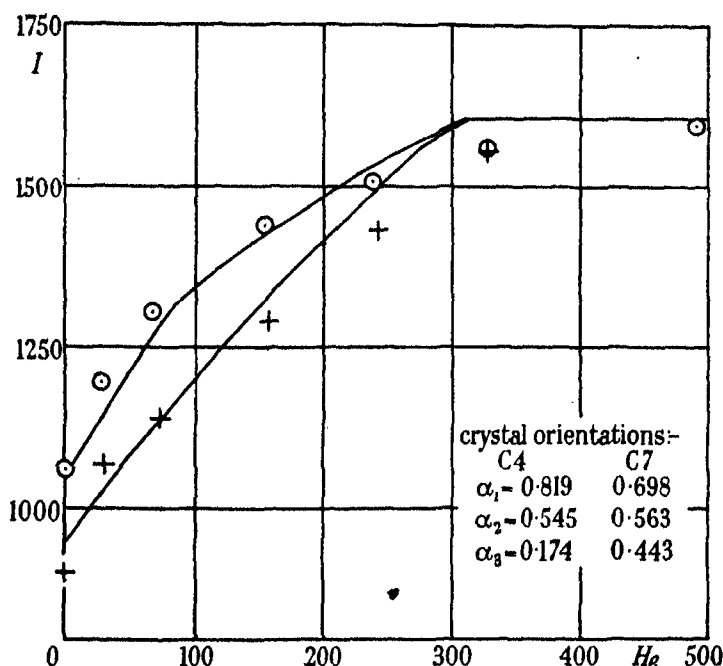


FIGURE 7. Calculated magnetization curves for long rods (iron-silicon), with orientations corresponding to our specimens C4 and C7. Experimental points (corrected for longitudinal demagnetizing effect) are also shown. Magnetization, I , in gauss, applied field, H_e , in oersteds.

It will be seen that the agreement between theory and experiment is not perfect. In our own measurements, the uncertainties of experiment, particularly the correction for air flux in the search coil were rather large but probably not quite sufficient to account for the whole of the deviation from theory. The differences can probably be attributed to imperfections in the crystals, leading to an appreciable strain energy term which should appear in equation (1). Corrections for strains can be made using an experimental [111] curve in a similar manner to that described for the oblate spheroid. The only [111] curves that are available are, however, ones such as those

of Honda & Kaya (1926) or Williams (1937) which were measured on specimens from quite different batches of material, where the strains may differ considerably from those in the long rods whose magnetization curves are to be corrected. The curves cannot therefore be corrected at all accurately without more data.

APPENDIX

Néel's paper is in three parts; the first covers much of the same ground as the present paper while the other two develop the details of domain structure required by the considerations of the first part and show that these afford a satisfactory explanation of many observations on Bitter patterns. In the first part Néel points out that the number of 'phases' (different directions) of magnetization that can exist in a crystal depends on the direction of the resultant field. The magnetization curve is interpreted as being made up of 6-, 3-, 2- and 1-phase regions successively, corresponding to $H = 0$, H in a $[111]$ direction, H in a $[110]$ direction and arbitrary H respectively. This leads to equations for the magnetization curves of oblate spheroids and long rods which are identical with those we have obtained except that we have treated the 2-phase region of the long rod more exactly than Néel. We have also dealt rather more fully than Néel with the action of the demagnetizing field in ensuring a symmetrical direction of H and with the errors introduced by various approximations in the theory.

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On the inhomogeneity of plastic deformation in the crystals of an aggregate

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[Plates 1 and 2]

The variation of plastic deformation in aluminium specimens consisting of large crystals has been determined by measuring elongation and hardness at various points after tensile deformation. The deformation varied from grain to grain, and also within each grain the deformation near the boundary was greater or smaller than at the centre according to whether the neighbour was more or less deformed, i.e. there is not necessarily inhibition of slip near grain boundaries. These results were supported by metallographic and X-ray observations. Their importance with respect to the calculation of the stress-strain curve of aggregates from those of single crystals is discussed. It is suggested that a mechanism other than slip operates near the grain boundaries during deformation, and even within the crystals during large extensions.

INTRODUCTION

Any theory of plastic crystal aggregates requires a knowledge of the behaviour of the crystals during deformation and of their interaction. Whereas the behaviour of single crystals under stress is well known, the effect of their interaction is not yet quite understood. Obviously, a crystal embedded in other crystals deforms differently from a crystal which is free from any constraint by neighbours. Such differences have been studied, particularly in aggregates of large-grain size, and the effect of the boundaries has been stated to consist in inhibition of slip.

Carpenter & Elam (1921) observed that during tensile deformation of coarse-grained aluminium the crystals exerted a supporting effect on each other. The deformation at the boundary was much less than in the centre of the crystals, and this effect was still noticeable at a distance of 0.25 in. from the boundary. Moreover, they noted that 'a crystal which narrowed on pulling in contact with one which remained broad tended to make the latter narrow also. In its turn, the crystal which remained broad, tended to prevent the other one from narrowing.'

In subsequent investigations only the fact that the boundaries restrict plastic deformation has been considered. Aston (1926) found that the change of crystal orientation during deformation is less near a grain boundary than at the centre of a crystal. His conclusion that the extent of deformation is correspondingly smaller near the boundary does not seem to be justified, since deformation due to multiple slip gives rise to a smaller change in orientation than the same deformation due to single slip. The diffuseness of the X-ray interferences usually increased as the boundary was approached indicating a greater amount of bending of the lattice planes.

Yamaguchi (1927) determined the local elongations from marks scratched on the surface of aluminium specimens. He found that 'the elongation at the boundary is always smaller than that of the adjacent crystals', although some of his evidence contradicts this statement.

The conclusion reached from all these investigations was that less deformation occurs near a grain boundary than in the centre of a grain. This slip interference producing an increased resistance to shear has been cited as an explanation of the higher hardness observed for aggregates compared to single crystals. The only quantitative investigation of this strengthening effect was carried out by Chalmers (1937). He measured the elastic limit of bicrystalline specimens of tin and found it to increase approximately linearly with the angle between the tetragonal axes of the two crystals. The area of the boundary did not influence the extent of strengthening, and 'the critical shear stress is raised by the proximity of a boundary, and the amount of slip that takes place is decreased'.

Chalmers's experiments clearly show that the change in orientation at the boundary is the important factor for the strengthening effect. The change in orientation also gives rise to different deformations within a crystal at different distances from the boundary. Barrett & Levenson (1940) have drawn attention to this inhomogeneity of the deformation. They have shown the existence of deformation bands which indicate that various parts of a crystal suffer different deformations.

The present investigation was undertaken to obtain quantitative data on the extent of the inhomogeneity and to ascertain whether the deformation is always restricted near the grain boundaries.

EXPERIMENTAL PROCEDURE

(a) *Preparation of specimens*

The material used was commercial aluminium of 99.15 % purity, the main impurities being Fe 0.5 % and Si 0.28 %. Tensile specimens having gauge length $6 \times 1 \times \frac{1}{8}$ in. were prepared with a grain size of 1 to 3 cm. These were first annealed at 200° C and back-reflexion Laue diagrams made to determine the orientation of the various grains relative to the specimen axis. One face of each specimen was mechanically polished and the specimens annealed again at 200° C. The final surface preparation was by electrolytic polishing, leaving a strain-free surface.

On this surface the grain boundaries could be seen microscopically as fine lines, but to facilitate their location the specimen was very lightly etched. Inclusions of impurities were present, but they were not preferentially distributed at grain boundaries.

(b) *Hardness measurements*

Three types of indentation hardness measurement were attempted:

- (i) Knoop diamond, load 25 g.
- (ii) Vickers diamond, load 200 g.
- (iii) Vickers diamond, load 1 kg.

It was found that the first two of these types were not useful after deformation of the specimens, as surface rumpling caused a wide scattering of the results which were not reproducible. Measurements with the Vickers diamond and 1 kg. load were much less sensitive to this effect and were later used exclusively. The probable error of these hardness measurements was calculated as less than 0.3 hardness unit, i.e. approximately 1.5 %.

Hardness before deformation was measured by making a straight line traverse of hardness indentations parallel to the axis of subsequent tensile deformation. The least distance between any two impressions was approximately five times the length of the diagonal of an impression.

The distance apart of the impressions was measured with a cathetometer to ± 0.001 cm., illumination being arranged so that one face only of the pyramidal impression reflected the light source. This gave a convenient and accurate reference line which was independent of the size of an impression.

(c) *Measurement of local deformation and hardness*

The specimens were then deformed in tension to 5 % elongation. The known distances between hardness impressions made *before* deformation were now used as gauge lengths and remeasured after deformation. The elongations of individual grains and of various areas within particular grains were calculated from the differences between distances measured before and after deformation. The error in each measurement of length was ± 0.001 cm., and hence in determining elongation on a gauge length of 2 mm. the error in the value for percentage elongation was ± 1.0 , and correspondingly larger for smaller gauge lengths. The extent to which elongation measurements could be localized was limited by this factor.

In order to determine the hardness after deformation a traverse of indentations was made parallel to the one made before deformation. Finally, Laue diagrams were made at several points suggested by the results obtained in the elongation and hardness measurements.

One specimen was then further deformed in tension to 17 % total elongation and the local deformation measured as before.

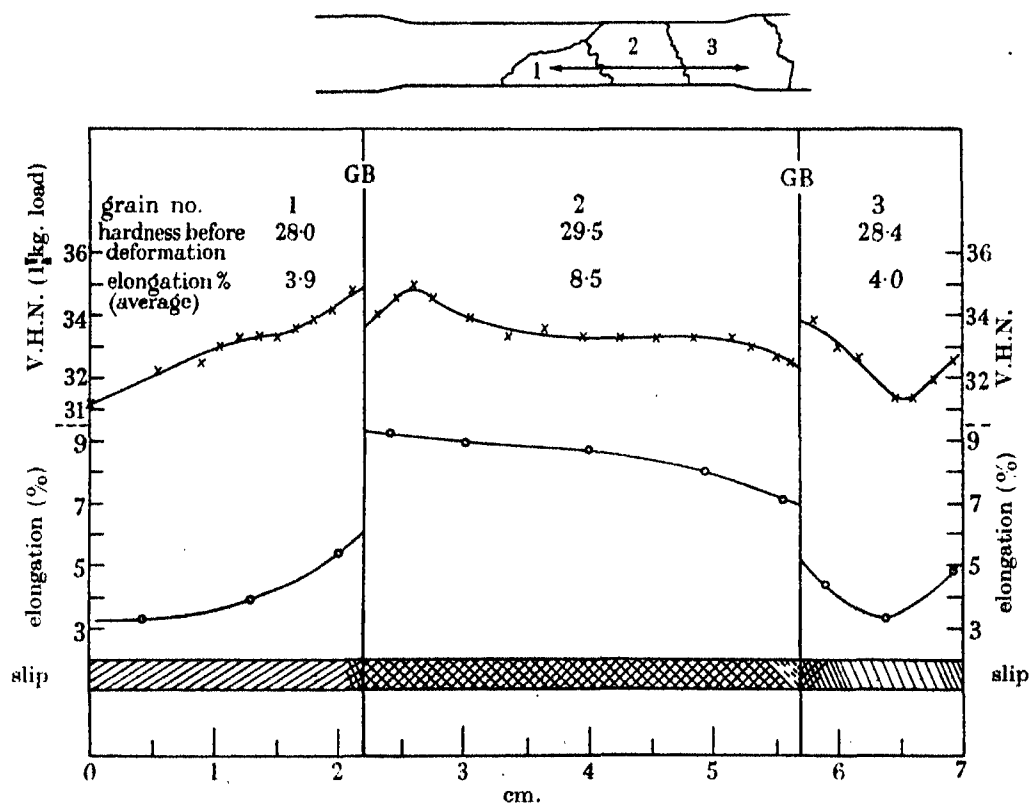
RESULTS

Typical of the results obtained are those for two specimens shown in figures 1 and 2. Hardness after deformation and percentage elongation are plotted against distance on the specimen. The values for elongation are plotted in the centre of the gauge length on which they were measured, and where possible a smooth curve is drawn. The heavy vertical lines represent the positions of grain boundaries; the grain numbers refer to the diagrams showing the surface configuration of the grains in the specimen. Also tabulated for each grain on the graph are the mean hardness value before deformation and the mean elongation. Hardness before deformation was constant in any grain within the limits of experimental error. The type of slip bands observed in various areas is indicated schematically in figure 1*a*.

It is obvious from the curves that the overall elongation of 5% given to the specimen produces widely different elongations in the individual grains. Moreover, the deformation is not uniform within one grain. As a boundary is approached the deformation becomes larger than at the centre if the average deformation of the neighbour is larger, and in the neighbour the deformation is less near this boundary than at its centre. This feature is even more apparent in the specimen which was extended by another 12% (figure 2). The elongations which are so different in the central portions of the grains become similar near the boundaries.

It can also be seen that the curves for hardness after deformation have the same trend as the elongation curves. Since hardness before deformation was constant within any grain, the curves for hardness after deformation indicate the distribution of work hardening and therefore of deformation *within one grain*.

The hardness measurements thus complement the observations made above with respect to the effect of the neighbour and give a better indication of the local deformation than the elongation measurements. The latter are average values over their respective gauge lengths, and the extreme variations thus obtained are therefore smaller than the actual variations. However, the degree of work hardening cannot



(a)

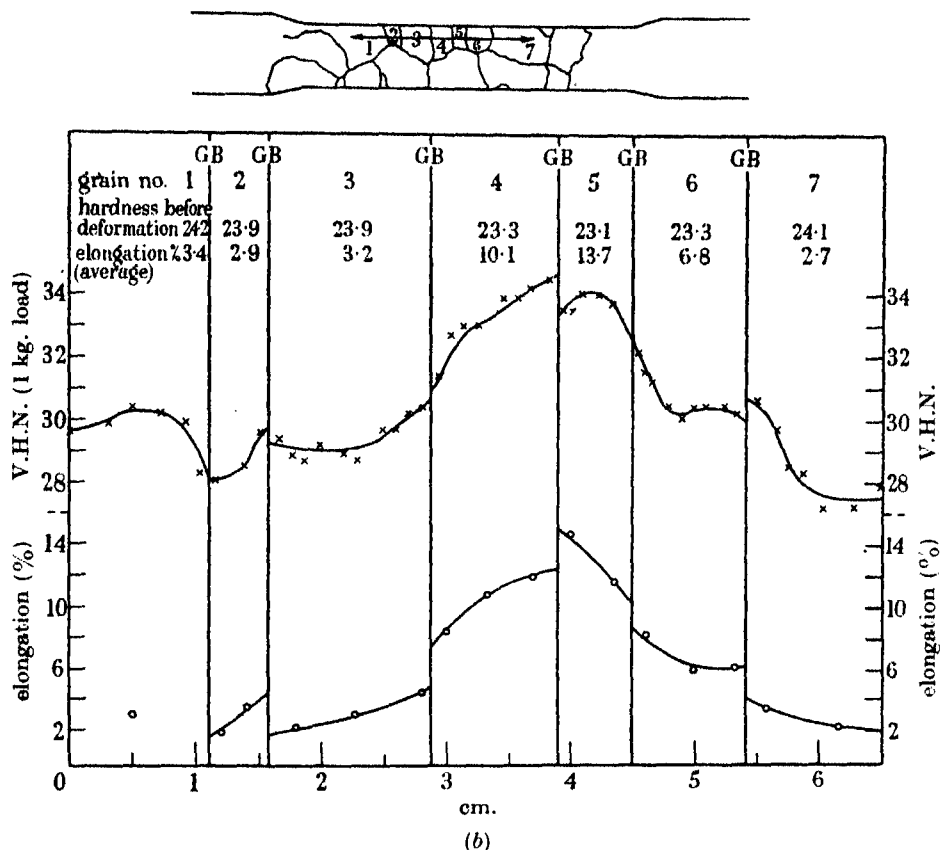


FIGURE 1. Hardness and local elongation of the grains of an aggregate after 5% elongation. (a) Specimen 19. Slip occurring at various points in the grains is shown schematically. (b) Specimen 5.

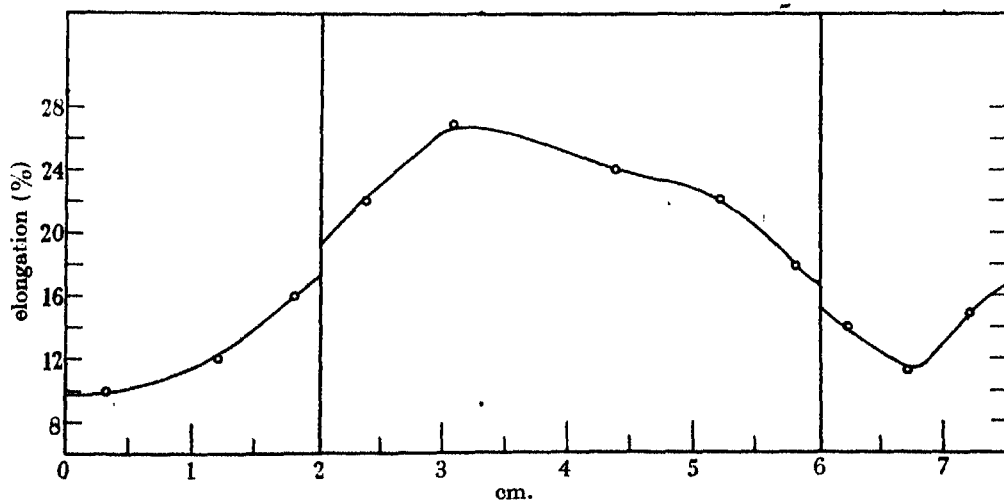


FIGURE 2. Local elongation of the grains of an aggregate after 17% elongation. Specimen 19.

be used to compare the degree of deformation of various grains as the rate of work hardening varies with the orientation of the grain.

These results are further supported by the evidence from microscopic observation of slip lines. The density of slip lines varies within a grain in a manner consistent with the elongation and hardness values for the grain. Where these measurements indicate more deformation near the boundary of a grain relative to the centre, the slip lines become more closely spaced as the boundary is approached and sometimes double slip appears. Similarly, when approaching a boundary where less than average deformation is indicated slip lines are wider spaced, and sometimes where double slip occurs throughout the grain it is replaced by single slip. These features are illustrated by figures 3 and 4, plates 1 and 2. Finally, the inhomogeneity of deformation is confirmed by observation of the spots in the Laue diagrams made at various points in the grains. The spots are more diffuse in diagrams resulting from areas where high deformation is indicated by the other measurements.

CONCLUSIONS AND DISCUSSION

From the experimental evidence the following conclusions can be drawn:

(1) During plastic deformation of an aggregate there are wide differences in the amount of deformation and work hardening from grain to grain. The overall extent of deformation and the average hardness of the aggregate do not indicate the behaviour of individual grains.

(2) Deformation is also inhomogeneous within each grain and corresponding hardness variations due to work hardening occur.

(3) The inhomogeneity of deformation is due to interaction of neighbouring grains and may extend up to 1.5 cm. from the grain boundary. The direction of this deformation variation is such that the deformation approaches that of the neighbour, i.e. the deformation tends to be continuous across the boundary.

The question now arises as to what determines the average deformation of a grain. No correlation could be established with the hardness before deformation. Although an indentation is produced by the same general process as elongation, i.e. by slip, the particular slip systems operating and the stress conditions are quite different, and hence the lack of correlation is not surprising. One would rather expect the original orientation of the crystal to be important in determining the average deformation of a grain. For purely tensile deformation the ratio of shear stress along the slip system to the external stress is given by the function $\sin \chi \cos \lambda$, where χ and λ are the angles between the direction of tension and the relevant slip plane and direction respectively. If that system acts, along which the shear stress is a maximum, the corresponding value of this function should express the susceptibility of a grain to deformation as determined by its orientation, for not only is the shear stress acting on the system proportional to this function but also the elongation for a given amount of shear. In figure 5 the maximum values of $\sin \chi \cos \lambda$ for the grains represented by figure 1 have been plotted against the average elongations

of the grains. Also plotted from the results of Karnop & Sachs (1927) are the elongations of single crystals of appropriate orientations under the same tensile stress as was used to deform the aggregates in the present experiments.

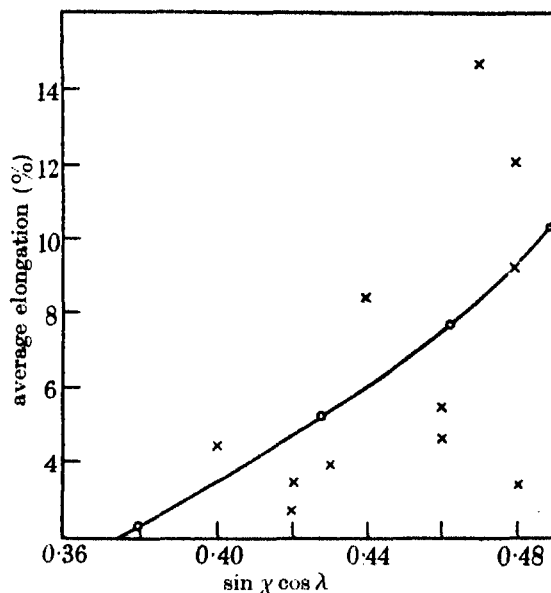


FIGURE 5. Elongations of crystals under the same external stress as a function of their orientation. $\times$ Average elongation of crystals in aggregates as observed in these experiments after 5% overall elongation. $\circ$ Elongation of free single crystals observed by Karnop & Sachs.

Two features are evident:

(a) While grains of high average elongation are grains for which the value of the function $\sin \chi \cos \lambda$ is high the converse is not true.

(b) The points for grains in the aggregates lie about the curve for single crystals under the same stress.

These observations lead to the conclusion that the distribution of stress in the aggregate is not uniform, some grains receiving more and some less than the externally applied stress. Thus while the product $\sin \chi \cos \lambda$ determines the susceptibility of a grain to deformation under a pure tensile stress, the geometry of the aggregate influences the actual stress on the grain and thus the extent of its deformation.

The observations are also of interest with respect to the calculation of the stress-strain curve of polycrystalline materials from the shear hardening curve of the single crystals. The only self-consistent calculation has been carried out by Taylor (1938) for aluminium, and gave good agreement with the observed tensile curve. However, as Barrett & Levenson (1940) have pointed out, the change of orientation of approximately one-third of the crystals in the aggregate is not that predicted by Taylor's theory. This lack of agreement must be due to the assumptions made. The main assumption on which the theory is based is that the material deforms uniformly

irrespective of the presence of grain boundaries and differently orientated grains. The present investigation has shown that not only are there differences in deformation from grain to grain, but also within any grain, thus contradicting Taylor's assumption.

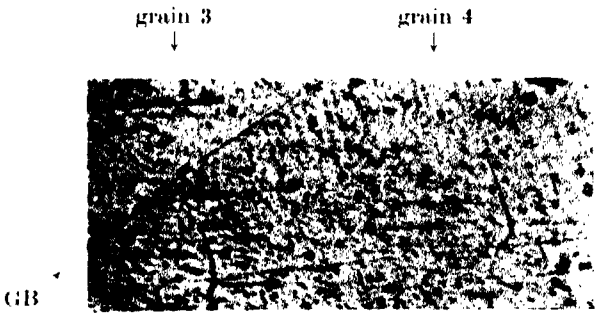
Before a new attempt to calculate the stress-strain curve can be made, the conditions prevailing at the grain boundaries have to be established. Certainly the slip is not homogeneous within a crystal, and it seems even to be doubtful whether slip is sufficient to explain the observed deformation. According to geometrical considerations any arbitrary deformation of a crystal, for instance, the deformation of a crystal in an aggregate, requires the occurrence of slip along at least five systems. Experimentally only single and double slip have been observed in our aggregates. Further, Barrett has shown that the change in orientation is not always such as would result if five-fold slip took place. Since contact at the grain boundaries is maintained slip cannot be the only mechanism of deformation operating in the crystals of an aggregate.

It appears that the deformation tends to be continuous at the boundaries, and if the deformation is entirely due to slip this implies quite different stresses on the two sides of the boundary where crystals of different orientations adjoin. Because of the principle of action and reaction the stress normal to the boundary and the shear stresses in the boundary must be continuous. Hence the mechanism of deformation must be such as to allow the deformation to be continuous, although the stresses are the same on the two sides of the boundary. In addition to the slip observed there must be another process for which the stress-strain relationship is different. The closer the approach to the boundary the greater is the relative proportion of the second process, although under favourable conditions more slip takes place near the boundaries than at the centre.

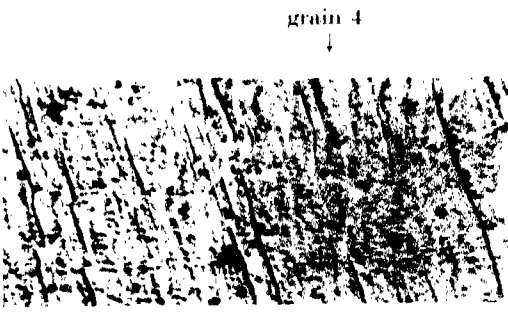
If five-fold slip were to operate at the beginning of plastic deformation the critical shear stress would have to be obtained on all five slip systems. The external stress necessary would be much higher than that which gives rise to the critical shear stress on the most favourable system for slip. It is suggested that non-slip deformation takes place at an external stress smaller than that necessary to initiate slip on the less favourably orientated of the five systems. No suggestion as to the nature of the non-slip deformation can yet be made from the experimental evidence.

Although in the present experiments only comparatively small deformations were used, it is considered that at higher deformations the non-slip mechanism will become increasingly important. The inhomogeneity observed for small deformations will penetrate further into the crystal as deformation proceeds, and at higher deformations the extent of the non-slip process will become greater. With smaller grain size the effect will be more pronounced. It has already been suggested by Chalmers (1940) that a type of plasticity similar to amorphous flow becomes preponderant at high deformations.

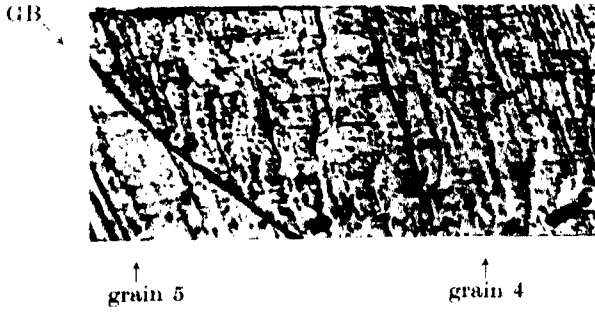
The results of this investigation were obtained from measurements on the surfaces of specimens. A crystal in the interior of a polycrystalline specimen will be still more



a



b



c

FIGURE 3

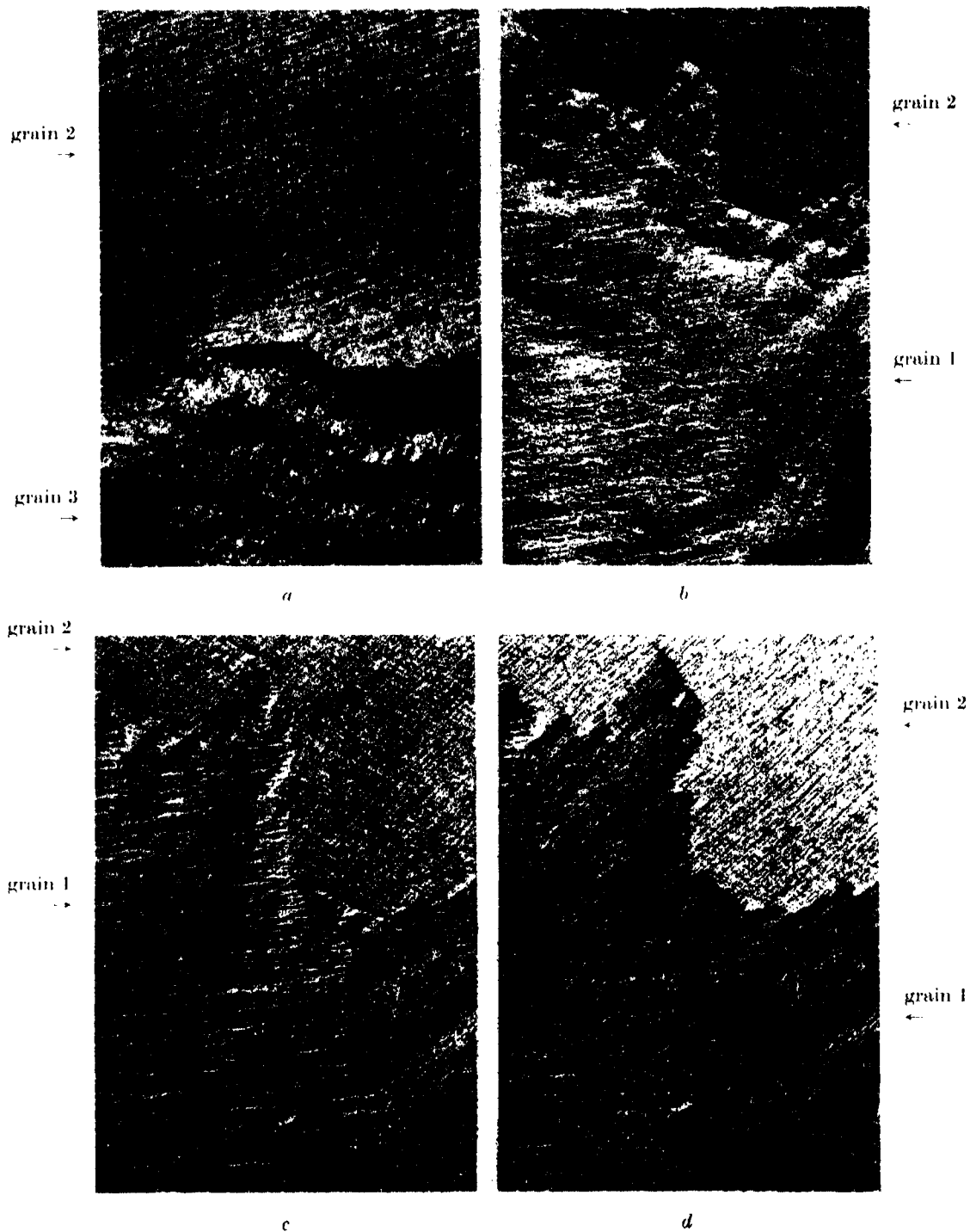


FIGURE 4

restricted in its deformation, since it is not allowed the freedom in deformation at the free surface (observed as surface rumpling) and has a larger grain-boundary area relative to its volume. For such a crystal the non-slip mechanism will therefore play a greater role than for a surface crystal. The continuity of deformation may then even extend throughout the crystals, and it is conceivable that the strain will become uniform in a small-grained specimen in agreement with Taylor's assumption. This uniformity, however, would be the result of the non-slip process.

This work forms part of a general programme, carried out by the Section of Tribophysics, Council for Scientific and Industrial Research, Australia. We wish to thank Professor E. J. Hartung for laboratory facilities in the Chemistry School, University of Melbourne, Professor H. K. Worner for the use of equipment in the Rosenhain Memorial Laboratory, and the staff of the Munitions Supply Laboratories Maribyrnong, for carrying out spectrographic analyses and help in the use of equipment.

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DESCRIPTION OF PLATES 1 AND 2

PLATE 1

FIGURE 3. Variation of slip line density in grain 4 of specimen 5 after 5% elongation. Compare with figure 1*b*. *a*, boundary area grains 3 and 4 ($\times 250$). *b*, centre of grain 4 ($\times 250$). *c*, boundary area grains 4 and 5 ($\times 250$).

PLATE 2

FIGURE 4. Slip lines in grain-boundary areas of specimen 19 after 5% elongation.

Compare with figure 1*a*.

- a*, boundary between grains 2 and 3. No double slip in grain 2 near the boundary ($\times 23$).
b, boundary between grains 1 and 2. Mainly single slip and surface rumpling in grain 1. Double slip in grain 2 ($\times 6$).
c, *d*, portion of the area shown in *b*, at higher magnification ($\times 15$). The same area is shown under different illumination in (*c*) and (*d*).
c, note the second slip system near the boundary in grain 1 in addition to the principal seen in *b*.
d, the extent of the second slip system in grain 1 is more apparent than in (*c*). The slip lines of this second system are almost parallel to those of one of the systems in grain 2.

An investigation of radio-frequency radiation from the sun

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It has been known for some time that the sun emits radio-frequency radiation whose intensity greatly exceeds the value expected from a black-body at 6000° K. In the present paper, experiments are described in which measurements have been made of the solar radiation at frequencies of 175 and 80 Mcyc./sec.

Measurement of the small powers which can be abstracted from practical aerial systems requires special types of receiving equipment if absolute measurements are to be recorded automatically over long periods of time. An apparatus has been developed in which the output power of a local source of random 'noise' is automatically and continuously adjusted so as to be equal to the aerial power; in this way the receiver is used only as an indicator of balance, and errors due to variation of its gain or internal noise are eliminated.

A special type of aerial has been devised which enables the solar radiation to be recorded separately from the galactic radiation, and so enables continuous observation of the sun to be made with aeriels of comparatively low directivity.

The results obtained on these two frequencies show that the sun normally emits radiation whose intensity corresponds to a surface temperature of the order of 10^6 °K. Large fluctuations in the intensity occur, however, and during the passage of large sunspots, equivalent temperatures as high as 10^8 to 10^9 °K have been observed. In addition to these day-to-day variations the radiation is subject to sudden brief increases of intensity lasting only for a few seconds.

Measurements of the diameter of the source, by a method analogous to Michelson's stellar interferometer, have shown that during periods of very great intensity the radiation originates in an area of the sun of the same order of size as a sunspot. This result means that equivalent temperatures of 10^9 to 10^{10} °K must exist.

Measurements of the polarization of the radiation have shown that during periods of increased activity the radiation is mainly circularly polarized.

The present account covers the experimental methods and the results obtained up to the present time. It is hoped to consider these results theoretically in a future paper.

1. INTRODUCTION

This paper describes some measurements which have been made on electromagnetic radiation emitted from the sun at radio-frequencies. When the work was started (October 1945), radiation from the undisturbed sun had been measured at frequencies of the order of 10,000 Mcyc./sec. (wave-length 3 cm.) by using an aerial of large equivalent aperture, having a narrow angle of reception (Southworth 1945; Sander 1947). It was also known that during the passage of large sunspots across the solar disk, radiation could be detected without the use of highly directive aeriels, on frequencies in the neighbourhood of 60 Mcyc./sec. (Appleton 1945; Hey 1946). The intensity under these disturbed conditions appeared to decrease as the frequency was increased; observation at frequencies less than 20 to 30 Mcyc./sec. was restricted by the effect of the terrestrial ionosphere.

If the radiation was received and amplified in a high-gain amplifier it appeared, in the telephones and on the screen of a cathode-ray oscilloscope, to have the

characteristics of the electrical 'noise', which is generated in a resistor. It was therefore natural to assume that the field of the wave was varying in a random manner, as if it were emitted from a source at a high temperature.

The intensity of the radiation from the undisturbed sun measured at a frequency of 10,000 Mcyc./sec. was approximately that to be expected from a 'black-body' source subtending an angle of $\frac{1}{2}^\circ$ at a temperature of 20,000° K. At this frequency, no increase of intensity at times of solar disturbance had been reported. Measurement of solar radiation on 60 Mcyc./sec. had only been reported when the sun was strongly disturbed; the failure to detect radiation at other times was presumably partly because the intensity was so small as to be masked by the electrical 'noise' in the amplifier, and partly because the general radiation from the galaxy masked any effect of solar radiation with the aerials of low directivity which were used.

In the experiments described in this paper, the aim was to make a more sensitive measuring apparatus, so that the solar radiation on a frequency of 175 Mcyc./sec. (wave-length 1.71 m.) could be measured continuously. This frequency was chosen because the correspondingly shorter wave-length provided the opportunity of constructing aerials having better angular resolving power, and yet it was not expected to be too high for the observation of the increased radiation found on lower frequencies during times of solar disturbance. Later, observations were also made at a frequency of 80 Mcyc./sec., and it is hoped, in the future, to extend the measurements to other frequencies.

Since, in any theoretical interpretation of the measurements, it is of fundamental importance to consider the temperature of the source, it is convenient to express the intensity of the radiation when it reaches the earth in terms of the equivalent temperature of a 'black-body' source situated at the distance of the sun, and subtending a known angle at the earth. In what follows, the intensity will frequently be expressed in terms of the equivalent temperature of a circular source of this kind, subtending the same angle as the visible solar disk (i.e. $\frac{1}{2}^\circ$). It is by no means implied, as will be obvious later, that the actual source of the radiation subtends this angle, but this method of describing the results proves to be useful when theoretical deductions are to be made. The power measured is that which can be abstracted from an aerial of given directivity, and the method of converting the result of this measurement into an 'equivalent temperature of a $\frac{1}{2}^\circ$ source' will be discussed in § 2.

The powers which are received in the comparatively non-directive aerials which have been used are quite small compared with the thermal power in the first circuit of the amplifier. It is therefore necessary to devise special circuits for the accurate measurement of the power from the aerial, and to consider in detail the limiting accuracy of such measurements. The fundamental principles which govern the operation of the system are discussed in § 3. The practical design of the apparatus is described in Appendix 1, and the limiting accuracy attainable with such equipment is derived. It is shown that an aerial power which is less than 1 % of that arising in the amplifier input circuit can be detected under the conditions encountered in practice.

The problem of distinguishing between the radiation received from the sun and from the galaxy is discussed in §4, and an aerial system which enables the solar radiation to be recorded separately is described.

The remainder of this paper is concerned with the experimental results obtained with apparatus working at frequencies of 175 and 80 Mcyc./sec.

During the period covered by these experiments, it is natural that similar observations should have been made by other workers investigating radiation from the sun on radio frequencies. Particular reference is made to the results obtained by the following workers:

(a) Pawsey, Payne-Scott & McCready (1946); Lovell & Banwell (1946); Dicke & Beringer (1946).

(b) McCready, Pawsey & Payne-Scott (1947) and Covington (1947); on the area of the source of increased solar radiation.

(c) Appleton & Hey (1946a) and Martyn (1946); on the polarization at times of great intensity.

The present paper is restricted to an account of our experiments and the results obtained. It is hoped to consider the interpretation of these results in a future paper.

2. THE EXPRESSION OF RANDOM E.M.F.'S IN TERMS OF TEMPERATURES

In much of the work on this subject it has been usual to express the results in terms of the mean power flux at the receiver. As already explained, it is thought more convenient to express the received power flux in terms of the temperature of a hypothetical source which subtends at the earth an angle equal to that of the solar disk. In this section it is shown how this temperature can be deduced from measurements in which the radiation received on a moderately directive aerial is compared with the power originating in a local source of electrical 'noise'.

It is first recalled that, according to Nyquist (1928), the available power which may be abstracted from a resistance at a temperature T is given by the expression $kT\delta f$, where k is Boltzmann's constant and δf the frequency band over which the energy is integrated. Similarly, the power which may be abstracted from an aerial mounted in a black-body enclosure at a temperature T is also given by $kT\delta f$ (Burgess 1941). If such an aerial is connected by a matched transmission line to a resistance, equilibrium will be attained when the resistance is at the same temperature as the enclosure. By adjusting the temperature of the resistance until no power flows, it is thus theoretically possible to determine the temperature of the enclosure.

Simple thermodynamic arguments indicate that the state of affairs is not altered if the aerial is directive; equilibrium is still maintained when the temperature of the resistance equals that of the enclosure. If, however, instead of receiving radiation from an enclosure, the directive aerial is irradiated from a black body at a temperature T_s , which subtends a solid angle ω , then in order to maintain equilibrium between the resistance and the aerial, the temperature of the resistance must be adjusted to a new value T_A which depends on the directivity of the aerial. If $f(\theta, \phi)$

represents the receptivity of the aerial per unit solid angle in the direction (θ, ϕ) compared with the receptivity in the direction of the source (and assumed to be constant over the area of the source), then T_A is given by

$$\frac{T_A}{T_s} = \frac{\omega}{\Omega}, \quad \text{where} \quad \Omega = \iint f(\theta, \phi) d\theta d\phi.$$

(The quantity $4\pi/\Omega$ corresponds to the power gain of the aerial in the direction of the source, compared with that of an isotropic radiator.)

The quantity T_A will be known as the 'equivalent aerial temperature', and represents the temperature of the attached resistance when equilibrium is established.

3. THE MEASUREMENT OF SMALL RANDOM E.M.F.'S

In order to measure the small powers available from the aerial system, it is necessary to use an amplifier whose input circuit itself gives rise to thermal e.m.f.'s corresponding to an effective temperature which will be denoted by T_R . In the absence of an input from the aerial, the deflexion of the output indicator varies in a random manner about a mean value which corresponds to T_R . The instantaneous deflexion may have any magnitude, but the mean value obtained from a large number (n) of instantaneous readings departs from the true mean by an amount proportional to $1/\sqrt{n}$. If the time constant of the circuits preceding the output indicator is t_i , then it is possible to obtain $1/t_i$ independent readings per second. If the time constant of the output indicator itself is increased to t_o , the output indicator will record an average over the time t_o , so that it will record effectively a number $n (= t_o/t_i)$, of independent readings. Then, by the previous analysis, it can be seen that the reading will fluctuate about the true mean value by an amount proportional to $1/\sqrt{n} = \sqrt{(t_i/t_o)}$. It is often more convenient to consider the band widths $\delta f_i = 1/t_i$ and $\delta f_o = 1/t_o$ of the circuits, and the fluctuations about the mean may then be expressed as proportional to $\sqrt{(\delta f_o/\delta f_i)}$. A similar analysis has been made by Dicke (1946).

If now a small random e.m.f., corresponding to an equivalent aerial temperature T_A , is injected, the output deflexion will vary in a random way about a new mean value corresponding to $T_R + T_A$. The increase in the observed mean value can be detected if the fluctuations are less than this increase. It can therefore be seen that, apart from other considerations, the smallest value of T_A which can be detected can be reduced indefinitely by making the ratio of the band widths $\delta f_o/\delta f_i$ small enough. There are, however, serious practical limitations to this ratio. In the first place the input band width δf_i must be kept small compared with the centre frequency f_i , because one aim of the experiments is to investigate the variation of the intensity with frequency.* In the second place the time constant of the output circuit cannot be made too large, because it is desired to record rapid changes in the intensity of the radiation. In practice the maximum value of $\delta f_i/\delta f_o$ is about 10^6 , so that it should be possible to detect values of T_A which are of the order $10^{-3}T_R$.

* It will also be shown in §7 that a measurement of the diameter of the source requires a reasonably small band width.

In the frequency range 50 to 3000 Mcyc./sec. the lowest attainable values of T_R are of the order of 1000 to 6000° K. The limit of detection in this range is therefore of the order of a few degrees.

If an aerial system having an effective solid angle Ω is used for observing a source at a temperature T_s subtending a solid angle ω , the equivalent aerial temperature has been shown to be $T_A = T_s \omega / \Omega$. For a source subtending an angle of $\frac{1}{2}^\circ$ and, with aerials of reasonable size, ω / Ω lies between 10^{-4} and 10^{-5} for the lower frequencies, and 10^{-2} and 10^{-3} for the higher frequencies. The smallest measurable equivalent temperature of a source subtending an angle of $\frac{1}{2}^\circ$ is therefore of the order of 10^4 to 10^5 °K at 50 Mcyc./sec. and 10^3 °K at 3000 Mcyc./sec.

The practical achievement of such a sensitivity involves problems which are discussed in Appendix 1.

4. THE SEPARATION OF SOLAR FROM GALACTIC RADIATION

Radiation from the galaxy causes a simple aerial at a frequency of 175 Mcyc./sec. to have an equivalent temperature which never falls below about 200° K, whilst the corresponding figure for 80 Mcyc./sec. is about 1000° K. If accurate measurements of solar radiation are to be made, it is therefore necessary to use a sufficiently directive aerial system to provide, from the sun, an e.m.f. comparable with that produced by the galaxy. An aerial system of this kind would be inconveniently large at these wave-lengths, and would have the further great disadvantage that continuous rotation would be necessary for observation of solar radiation throughout the day.

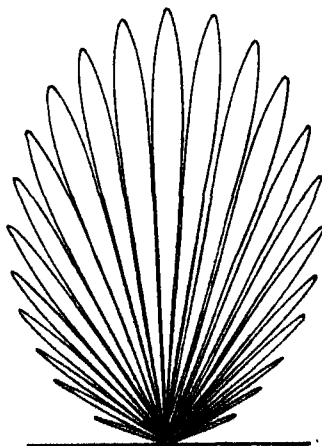


FIGURE 1. Interference pattern produced by two aerials separated by ten wave-lengths.

An alternative system has therefore been devised which allows continuous observation of the solar contribution separately from that due to the galaxy, without the need for a highly directive aerial. In this system two fixed aerials are used, separated by about ten wave-lengths, and situated on a line running east and west. Such an arrangement produces an interference pattern having minima separated by about 6° , as shown in polar co-ordinates in figure 1. When a source such as the

sun, which subtends a small angle, moves across such an interference pattern, the power received varies in a periodic manner from a minimum value, which is virtually zero, to a value twice that which would be received by a single aerial. On the other hand, a source, such as the galaxy, which subtends an angle large compared with the separation of the interference minima, gives rise to a nearly constant power. The solar contribution then appears on the recorded trace as a periodically varying signal, whose amplitude may be determined accurately even when it is smaller than the galactic component.

Practical details of the aerials used in this system are given in Appendix 2 (a), and a typical record obtained during a period of increased solar activity is shown in figure 2.

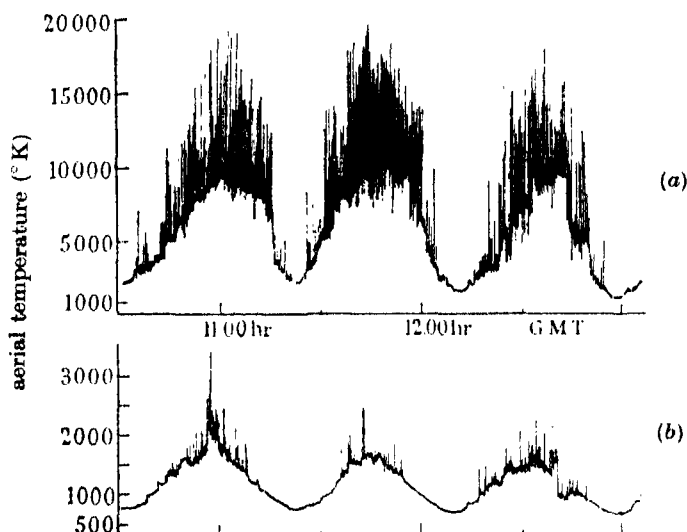


FIGURE 2. Record of solar radiation obtained with spaced aerial system. 25 January 1947. (a) 80 Mcyc./sec.; (b) 175 Mcyc./sec.

5. OPERATION OF THE COMPLETE SYSTEM

Details of the apparatus which has been designed for measuring the small e.m.f.'s available from the aerial system, are given in Appendix 1. The e.m.f. from the aerial is compared with that from a local source of noise power, and it is arranged that the latter is continuously and automatically varied to maintain a balance. A diode operating under temperature-limited conditions is used as the local source of noise power, and the output of such a generator is directly proportional to the mean anode current (Schottky 1922). The anode current may therefore be used as a measure of the power available at the termination of the aerial feeder and, after correction for the feeder losses (see Appendix 2 (a)), as a measure of the equivalent aerial temperature.

The anode current of the diode is therefore used to operate a pen recorder, which then gives a continuous record of the equivalent aerial temperature. By observing

the amplitude of the fluctuating component of this trace, as the spaced aerial system moves with the earth's rotation, it is possible to determine that part of the equivalent aerial temperature which is due to solar radiation.

It has been shown in § 2 that if the effective solid angle (Ω) of the aerial system is known, it is possible to convert the observed values of equivalent aerial temperature into the equivalent temperatures of a black-body source subtending an angle of $\frac{1}{2}^\circ$. The method of estimating Ω is discussed in Appendix 2 (a), and with this knowledge the readings of the recorder chart can be converted into 'equivalent temperatures of a $\frac{1}{2}^\circ$ source'.

This, in outline, is the system which has been used at frequencies of 175 and 80 Mcyc./sec. in the experiments to be described in the remainder of this paper.

6. THE TEMPORAL VARIATION OF INTENSITY

It is convenient to divide the discussion of the results into (a) short-lived 'bursts' of radiation, (b) sudden large increases of intensity, observed during periods of increased solar activity, and (c) the day-to-day variation of mean intensity observed over a period of several months.

(a) 'Bursts' of radiation

During times of increased solar activity the radiation is characterized by the presence of brief periods of increased intensity. These 'bursts', as observed on an apparatus having an output time constant of about half a second, usually last for 1 to 20 sec., and may have an intensity of 2 or 3 times the mean intensity at 175 Mcyc./sec. or 5 to 10 times the mean intensity at 80 Mcyc./sec. Examples of this type of burst can be seen in figure 2.

An examination of large numbers of such records has shown that there is apparently no correlation between the times of individual bursts of this type on the two frequencies.

(b) Sudden increases of the radiation

At times there are sudden large increases of intensity, which may attain values 10 times (for 175 Mcyc./sec.) and 20 to 100 times (for 80 Mcyc./sec.) the mean intensity and may last for many minutes. Whilst it is probable that no real distinction can be drawn between these disturbances and the small bursts described above, it is usual for the larger increases to be observed on both frequencies although the time of commencement may differ by a few minutes. It is also common for these sudden increases to be associated with solar flares and the 'catastrophic' type of ionosphere disturbance which produces radio fade-outs on short waves and enhancements on very long waves. A typical example of a sudden increase is shown in figure 3.

(c) Day-to-day variations of mean intensity

The equivalent temperatures of a $\frac{1}{2}^\circ$ source (see § 2) averaged over the four midday hours of each day, are plotted in figure 4 for the period covered by our observations. It is first of interest to consider the ratio of the intensities at the two frequencies

and the ratio of the equivalent source temperatures (T_{80}/T_{175}) is also plotted in figure 4. A comparison of these curves shows that the departure from the mean value of the source temperatures at either frequency is notably greater than the departure from the mean of the ratio of the source temperatures. It is therefore concluded that the day-to-day variations of intensity at the two frequencies are to

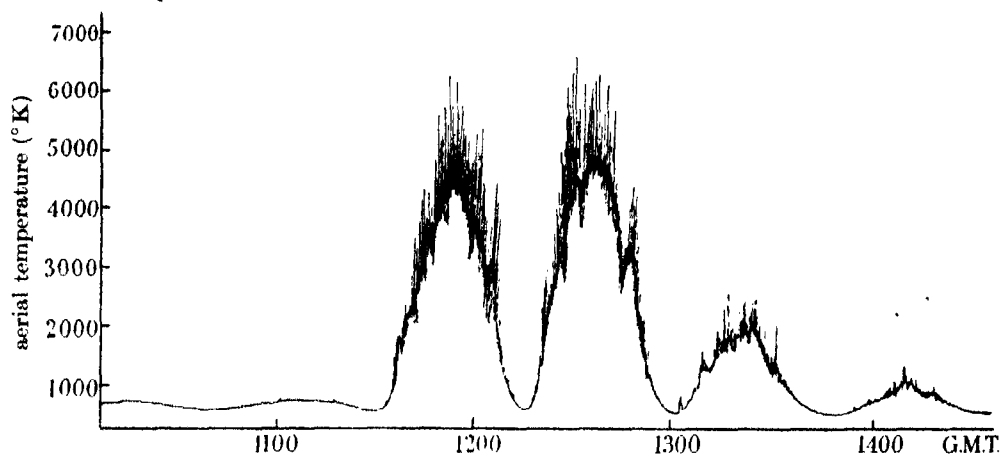


FIGURE 3. Sudden increase of intensity observed at 175 Mc/sec. 4 March 1947.

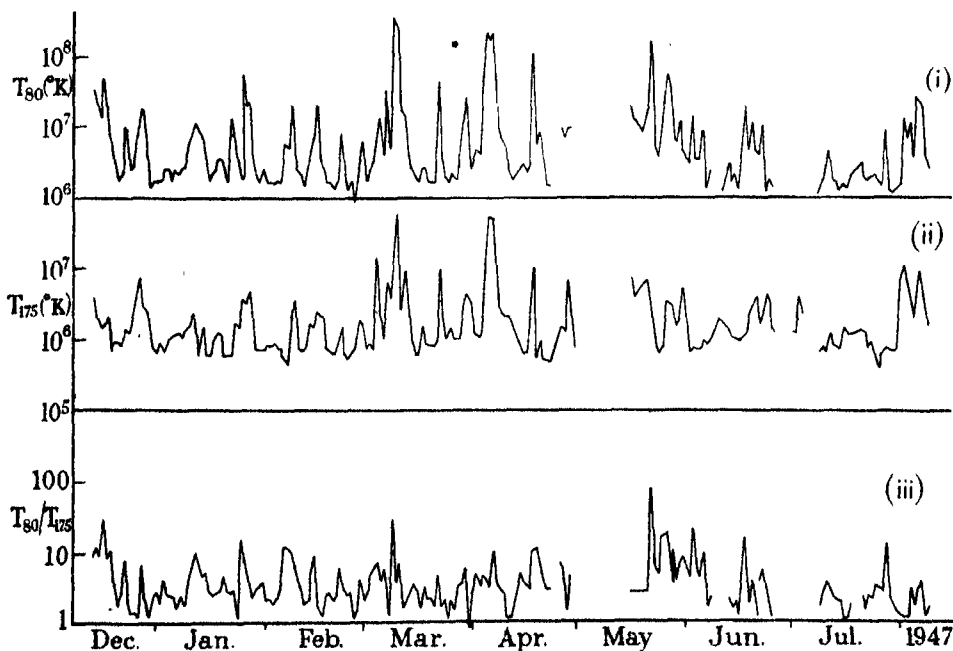


FIGURE 4. Day-to-day variation of equivalent $\frac{1}{2}^\circ$ source temperature. Curve (i) 80 Mc/sec. (T_{80}); (ii) 175 Mc/sec. (T_{175}); and (iii) ratio of 80 and 175 Mc/sec. (T_{80}/T_{175}).

some extent related, although on some occasions the intensities may show independent variations.

It can be seen from figure 4 that the long-term average of the ratio T_{80}/T_{175} is of the order of 4, which is in accord with previous suggestions that the equivalent temperature of the source is proportional to the square of the wave-length. There

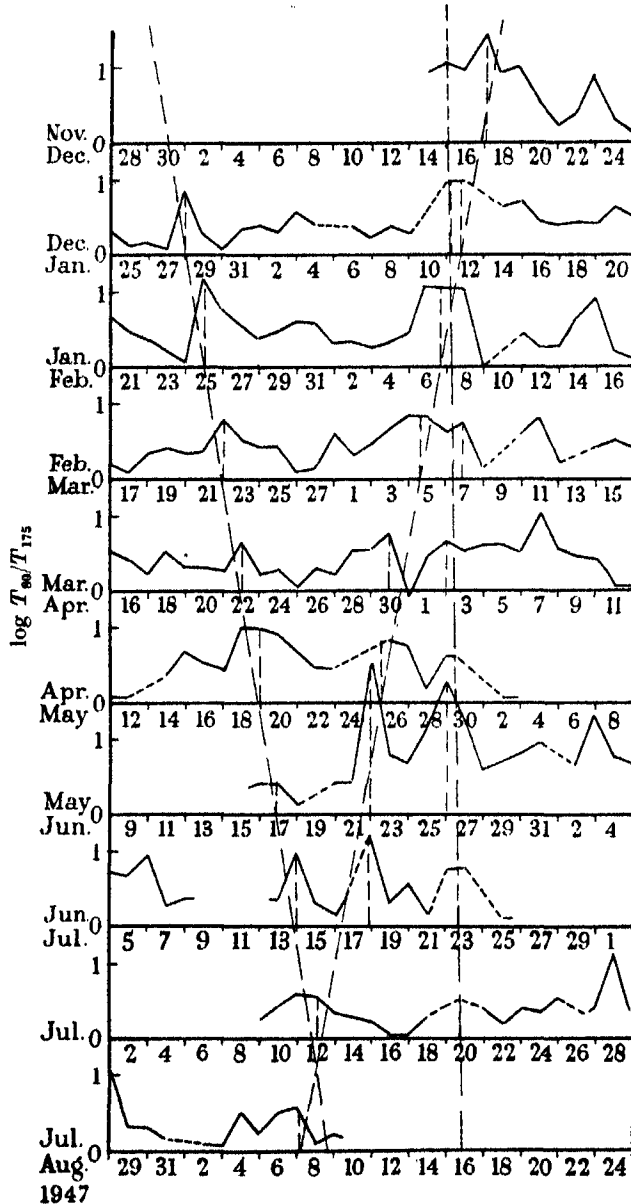


FIGURE 5. Curve showing periodic variation of T_{80}/T_{175} .

is, however, a marked variation about this value, which must represent a true change of the ratio of the intensities and cannot be the result of selective effects of the ionosphere (as originally suggested by Appleton & Hey (1946*b*), since any such effect would be inappreciable at these frequencies.

There is a suggestion, in figure 4, of a 27-day recurrence tendency in the ratio T_{80}/T_{175} , such as might be associated with the period of rotation of the sun. In order to show up this tendency more clearly, the ratio curve in figure 4 has been plotted in a different manner in figure 5. The apparent periodicities of 28, 27 and 26.3 days noticeable on the diagram might be attributed to the presence of active regions at different solar latitudes, since it is known that the rotation period depends on the latitude. Since the main departures from the mean value shown in figure 5 have a duration of the order of 2 to 3 days, any explanation would involve the assumption of directed emission of the radiation with an angular distribution which was different at the two frequencies. It has already been suggested that the results shown in figure 4 lead to the conclusion that the day-to-day variations at the two frequencies are to some extent related, and if the recurrence tendency of figure 5 is substantiated by further measurements, the results will seem to suggest that the intensity of the radiation at the earth is determined jointly by:

- (i) the general excitation conditions, which affect both frequencies in a similar manner, and are apparently of a random nature, and
- (ii) the angular distribution of the radiation emitted by the sun, which may be different at the two frequencies.

7. MEASUREMENT OF THE DIAMETER OF THE SOURCE

In July 1946 the solar radiation became, for a short time, unusually intense, and the opportunity was taken to measure the diameter of the source at a frequency of 175 Mcyc./sec. The method adopted was an extension of the spaced-aerial system used to eliminate galactic radiation. By increasing the spacing between the aerials, the angular separation between the minima of the interference pattern can be progressively decreased, and when this angle becomes comparable with the angular diameter of the source, the received e.m.f. no longer falls to zero at the minima. By measuring the ratio of maximum to minimum e.m.f. obtained with a series of different aerial spacings, the effective diameter of the source can be determined. This method is analogous to Michelson's method for determining stellar diameters, the spaced aerials taking the place of the spaced mirrors, and the observed values of maximum to minimum corresponding to the 'visibility' of the interference fringes in the optical case.

The experiments were carried out using two arrays (each of eight half-wave dipoles in front of a reflecting screen) mounted on an east-west line, with the axes of maximum gain aligned on the sun at noon. Observations were made with spacings of 25, 90 and 140 wave-lengths; a typical record obtained with a spacing of 140 wave-lengths is shown in figure 6.

With a fixed spacing between the aerials, a small change of frequency will cause a shift of the interference pattern at angles away from the axis of the system (south). Owing to the finite width of the frequency spectrum which is accepted by the amplifier, the maximum to minimum ratio observed when the sun is at an appreciable angle from south will therefore be less than the true value corresponding to the diameter of the source. Calculation shows that for a spacing of 140 wave-lengths and a band width of 2 Mcyc./sec., observations must be made within 40 min. of noon. This effect is analogous to the production of coloured fringes away from the axis of an optical interferometer.

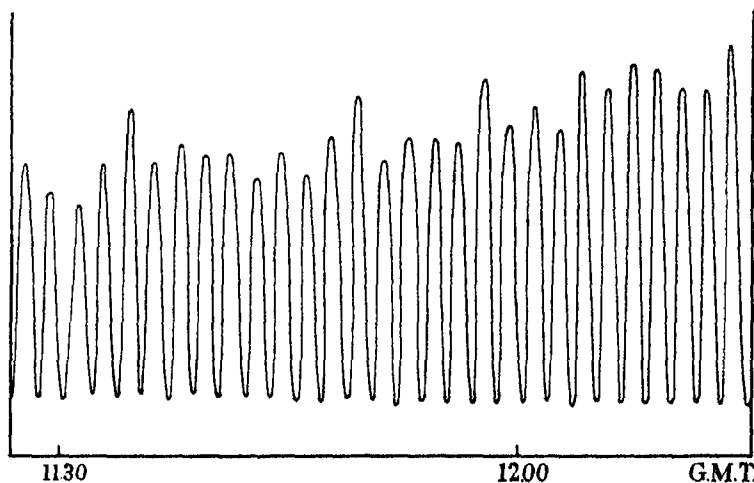


FIGURE 6. Record obtained with aerial spacing of 140 wave-lengths. 26 July 1946.

After subtracting the galactic contribution (obtained from records using a small aerial spacing) from records of the type shown in figure 6, the midday value of the maximum to minimum ratio corresponded to a source of diameter 10 min. of arc. The effects of impedance mismatch and unbalance in the aerial system are discussed in Appendix 2 (*b*), in which it is shown that such effects can only give rise to an overestimate of the diameter of the source. It is therefore concluded that the source of this intense radiation subtended an angle, in the east-west plane, not greater than 10 min. of arc.

This result indicated that the effective temperature of the source was considerably greater than that estimated for a source subtending an angle of $\frac{1}{2}^\circ$, and for radiation at a frequency of 175 Mcyc./sec. was at least 2×10^9 °K.

8. THE POLARIZATION OF THE RADIATION

(a) *Measurement of polarization*

Experiments have been made to determine the polarization of solar radiation at a frequency of 175 Mcyc./sec. Whilst the complete analysis of a mixture of polarized components requires a rather complicated experiment, preliminary measurements

with an aerial system capable of rotation about an axis normal to the wave front showed the absence of plane polarized components. In addition, it has been found that on most occasions when the intensity is large, the polarization is completely circular. Measurements have therefore been restricted to a determination of the intensities of the two circularly polarized components.

Two systems have been used; the first is a development of the spaced aerial system and is suitable for the accurate measurement of the degree of polarization even when the intensity is smaller than that due to the galaxy; the second is not suitable for quantitative measurements except when the solar radiation is large, but is rapid in operation and therefore provides information on the polarization of individual 'bursts' of radiation.

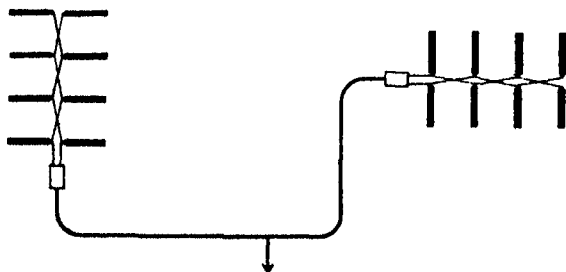


FIGURE 7. Interference polarimeter.

In the first method two simple linear aerials were used, spaced 10 wave-lengths apart and with their axes of polarization perpendicular to each other. Figure 7 shows how the arrangement would appear when viewed from the direction of the sun at midday. If the radiation incident on this system were randomly polarized, as from a source of pure thermal 'noise', the radiation received on the two aerials would be incoherent, so that the resultant power would not vary as the path difference from the source to the two aerials was altered. There would therefore be no periodic variation of the resultant power as the sun moved past the aerial system. The existence of a fixed phase relationship between the horizontal and the vertical components of the field in the incident wave would result in a periodic variation of the resultant power as the relative phase at the two aerials changed. The direction of the sun relative to the line between the centres of the two aerials, at the moment when the power reached a maximum enabled a distinction to be made between the incidence of right- and left-handed polarized radiation. By comparing the amplitude of the variation observed on the record with that obtained with two similar aerials having the same polarization (as in § 4), it was also possible to determine the extent to which the radiation was polarized.

In the second method, two aerial systems with perpendicular planes of polarization were mounted with their axes coincident, but displaced by a quarter of a wave-length in a direction normal to the incident wave front. If the outputs of these two aerials were combined, the incidence of a circularly polarized wave of one sense then gave an output power double that of a single aerial, whilst the incidence of a wave

of the opposite polarity caused complete cancellation, and no output power was obtained. By combining the outputs of the two aerials in such a way that an extra half wave-length was introduced in one path, the behaviour could be reversed, and the system could be made sensitive to the opposite polarization. For a randomly polarized wave, equal power outputs were obtained in the two arrangements. By comparing the powers obtained with the two methods of connexion it was therefore possible to determine immediately the sense, and the degree of circular polarization in the incident wave. In the presence of galactic radiation, however, it was not possible to assess the ratio accurately except when the intensity of solar radiation was large.

The results obtained with these systems at a frequency of 175 Mcyc./sec. have shown that at times of large intensity (associated with an increase of activity in a particular source region) the degree of circular polarization is nearly always complete. The sense of the polarization is different for different active regions and it is a possible conclusion that the radiation from any particular source is fully polarized; the simultaneous reception of radiation from two or more sources (as at times of no special activity) would then give rise to resultant fields showing incomplete polarization.

It has been found that in nearly all cases the polarization of the short-lived bursts described in § 6 (a) is of the same sense as that of the background radiation. This suggests that these bursts may arise from brief increases of the excitation of regions already responsible for the general radiation. It is possible that the general background of radiation is, in fact, the resultant of a large number of short bursts, only the larger of which can be resolved on an apparatus with an output time constant of the order of half a second.

(b) *Correlation with solar magnetic fields*

It is natural to suggest that the production of circularly polarized radiation is related to the magnetic fields of the sun, and in particular to the magnetic fields of sunspots which cause radiation of high intensity. It is of importance to seek a relation between the sense of the polarization and the direction of the field in the region of the source. It may be shown that a clear-cut correlation of this kind would enable a distinction to be made between two possible regions for the production of the radiation.

An attempt has therefore been made to relate the sense of the polarization to the sense of the magnetic field of the sunspot as determined by observations of the Zeeman effect. During the period of these experiments, sunspot activity was considerable, and it was usually not possible to locate, with certainty, the sunspot responsible for the increased radiation. In addition, the complex nature of the magnetic fields of most large sunspots usually made it necessary to know the position of the source region within the spot group. It was sometimes possible to make an estimate of the position of the source by observation of the variations of the intensity as the spot group crossed the meridian, but it is clear that a conclusive result is only

likely to be obtained by making a large number of such observations, or alternatively by using an aerial of high resolving power. Out of sixteen observations analysed in this way, nine corresponded to radiation having the polarization of the ordinary wave of Appleton's magneto-ionic theory for electrons, three corresponded to the extraordinary wave, and four were inconclusive. (For a sunspot having a magnetic dipole with its north-seeking pole directed away from the centre of the sun, the ordinary wave has left-handed polarization, i.e. the electric vector rotates anti-clockwise when viewed along the positive direction of propagation.)

9. SUMMARY OF EXPERIMENTAL RESULTS

It has been found that the sun at all times emits radio-frequency radiation whose intensity exceeds that expected from a source at 6000°K . The minimum intensity observed for frequencies less than 200 Mcyc./sec. corresponds to radiation from a black-body source at a temperature of the order of 10^6°K and subtending an angle of $\frac{1}{2}^{\circ}$. If the radiation can only escape from certain restricted areas of the solar disk, the equivalent temperature must be correspondingly higher.

During the appearance of sunspots, particularly when these are near the meridian, the intensity may be much increased, reaching values corresponding to a $\frac{1}{2}^{\circ}$ source at a temperature of the order of 10^8°K for 175 Mcyc./sec., and 10^9°K for 80 Mcyc./sec. radiation. Experiments have shown that the radiation under these conditions is emitted from a region whose size is of the same order as the visual sunspot. The source regions must therefore have equivalent temperatures of at least $2 \times 10^9^{\circ}\text{K}$ for 175 Mcyc./sec. radiation. Measurements of the diameter of the source at lower frequencies have not been made, but it is possible that still higher equivalent temperatures may be necessary to account for the observed intensities.

During the periods of greater activity, the radiation is characterized by sudden brief increases of intensity. These 'bursts' of radiation may have intensities as great as 100 times the mean value, with durations of a few seconds to many minutes. The larger bursts (which are usually observed nearly simultaneously on both 175 and 80 Mcyc./sec. and are often accompanied by other evidence of solar activity) may represent an increase in source area, but it seems probable that sudden increases of the equivalent temperature must be involved.

The radiation during periods of increased intensity has been found to be circularly polarized.

The authors wish to express their appreciation of the guidance and encouragement of Mr J. A. Ratcliffe throughout this work. We would also like to acknowledge the great assistance of Messrs K. E. Machin and H. M. Stanier and others in the Cavendish Laboratory in the design and construction of the experimental apparatus. For the supply of solar data and for much useful discussion we are indebted to Professor F. J. M. Stratton and the staff of the Solar Physics Observatory and to

Mr H. W. Newton of the Royal Observatory, and for providing special magnetic data we have to thank Mr S. B. Nicholson of the Mount Wilson Observatory.

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APPENDIX 1. THE DESIGN OF APPARATUS FOR MEASURING SMALL RANDOM E.M.F.'S

(a) *Practical difficulty of achieving theoretical sensitivity*

It was shown in § 3 that it is theoretically possible to detect e.m.f.'s very much smaller than the random e.m.f.'s originating in the input circuit of the amplifier used. (If T_A and T_R represent the equivalent temperatures of the signal and input circuit $T_A > \sqrt{(\delta f_o / \delta f_i)} T_R$, where δf_i and δf_o are the input and output band widths respectively.) The possibility of achieving such a sensitivity in practice will now be considered, with particular reference to the measurement of solar radiation, where automatic operation over long periods of time is necessary.

The use of a narrow band width filter on the output of a conventional receiver makes it possible to reduce the residual fluctuations of the output to a value which corresponds to the required limit of detection, but the mean value of the output is directly proportional to the receiver gain, and thus a change of gain of the order of 0.1 % will produce a comparable change of output reading. The maintenance of the gain of a high-gain amplifier to such an order of accuracy is not practicable without periodic calibration. In addition, a change of T_R (such as may occur as the result of ageing of the first valve) results in errors which are independent of those due to changes of gain.

These difficulties have been largely overcome by Dicke (1946) in a method which periodically replaces the aerial by a load resistance at room temperature. If the load resistance and aerial present equal impedances to the amplifier input, the amplitude of the square-wave output when such a switching is carried out at a high speed, provides a measure of the difference between room temperature and the equivalent aerial temperature.

The output reading is, however, still proportional to the gain of the receiver, which must therefore be kept constant. The output also depends on the law of the detector, and, in general, calibration of the apparatus is necessary. Any such calibration must be made with an e.m.f. having a wave form similar to that of the e.m.f. to be measured. The use of such a calibration source also renders it unnecessary to correct for variation of the amplifier gain across the band of frequencies accepted and is therefore desirable even when the law of the detector is known.

A method has been developed which overcomes these difficulties and, besides giving an output reading which is independent of the gain and frequency response

of the amplifier, and the law of the detector, has the additional advantage of being capable of operating over a wide range of input powers without the necessity for calibrated switching of the gain.

(b) *Description of the system adopted*

In this system a local source of noise power is continuously adjusted so as to be in equilibrium with the aerial. This adjustment is achieved by alternately switching the amplifier input between the aerial and the noise source. If the impedances of the aerial and the noise source are equal, equilibrium between noise source and aerial is attained when equal power flows at the amplifier input in the two switch positions. This condition is independent of the impedance and the equivalent temperature of the amplifier input. If the powers introduced from the aerial and from the noise source are not equal, the output of the detector will vary at the switching frequency, and this output voltage can be used to adjust the effective temperature of the noise source until equilibrium is attained. Such adjustment does not depend on the gain or frequency response of the amplifier, or on the law of the detector. Figure 8 is a schematic diagram of the system. The accuracy with which measurements can be made with such a system will be discussed in the next section.

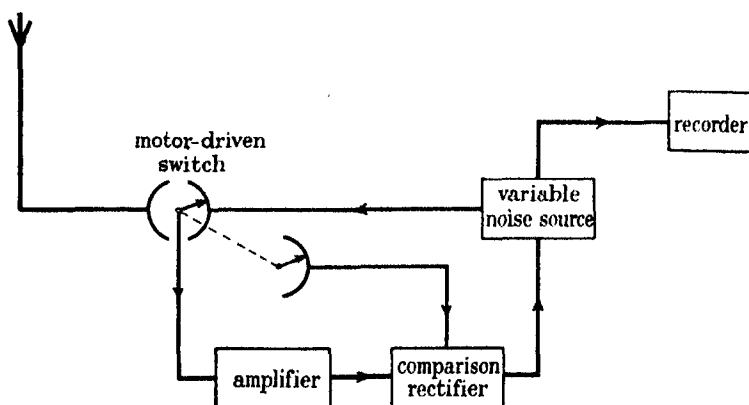


FIGURE 8. System for the continuous measurement of small radio-frequency powers.

In practice, the input powers involved are inconveniently large for production in a heated load resistance, and a diode operating under temperature-limited conditions provides a more convenient source of noise power, control of the output being achieved by adjustment of the filament temperature.

The r.m.s. noise current in a band width δf flowing in the anode circuit of a temperature-limited diode has been shown by Schottky (1922) to be given by the expression $\sqrt{2eI\delta f}$, where I is the mean anode current and e the electronic charge. If this noise current flows through a resistance r , the noise power generated in the resistance is given by $2eIr\delta f$. In order to provide a source of noise power which presents the same impedance as the aerial, it is necessary to terminate the feeder from the switch to the noise source in a matching resistance (R). The diode noise

current now flows through a resistance of $\frac{1}{2}R$, and the available diode noise power which can be abstracted from the feeder is given by $\frac{1}{2}eIR\delta f$, which corresponds to a temperature T_D of the terminating resistance given by

$$T_D = \frac{\frac{1}{2}eIR\delta f}{k\delta f} = \frac{eIR}{2k},$$

where k is Boltzmann's constant.

The total available power therefore corresponds to a temperature $T_0 + eIR/2k$, where T_0 is the actual temperature of the resistance.

The equivalent aerial temperature may thus be measured in terms of the mean anode current of the diode.

The operating range of the instrument may be altered by inserting an attenuator between the diode noise source and the change-over switch. The effective temperature of such a system can be shown to be $(T_D + T_0)\alpha + T_0(1 - \alpha) = T_0 + \alpha T_D$, where $T_D = eIR/2k$, T_0 = room temperature and α = power attenuation constant. Under these conditions the sensitivity, expressed in degrees per milliampere of diode anode current, is determined only by α , and if the gain of the amplifier is automatically maintained at the optimum value by a long time constant automatic gain control circuit, the change of the attenuation constant is the only adjustment required to change the operating range.

The finite time taken to alter the temperature of the diode filament results in a time lag in the correction of a misalignment between aerial power and diode power, and this may lead to instability of the system. This effect is analogous to the instability of all types of servo-mechanism containing 'inertia', and may be eliminated by applying to the diode filament an additional voltage proportional to the rate of change of the anode current.

(c) *Analysis of the accuracy of the system*

In this section the sources of error in the system will be considered and an estimate made of their magnitude.

(i) *'Following' accuracy*

In order to provide the necessary control voltage to the filament of the noise diode, a small misalignment must exist between the powers reaching the amplifier input from the aerial and from the noise source. The actual error in the mean recorded reading which is introduced depends on the preset bias voltage applied to the diode filament in the absence of an input signal, but the maximum error which can occur with any bias setting can be estimated.

If the overall gain of the amplifier is G , and the output voltage which must be applied to the filament of the diode to vary the noise output from zero to maximum is V , the maximum error in the recorded reading of equivalent aerial temperature is given by $\delta T_A = V/G$. It is therefore important that the overall gain should be as large as possible. The gain is limited by overloading of the output stage of the amplifier (on the assumption that the necessary conditions for stability—as discussed in the

previous paragraph—are satisfied). If the injected e.m.f.'s are small compared with the random fluctuations originating in the input circuit of the amplifier (i.e. $T_A \ll T_R$), the signal at the output stage consists of a steady voltage ($G\delta T_A$) due to the input misalignment, and a random fluctuation of approximately $GT_R/\sqrt{n}$, where $n = \delta f_i/\delta f_o$. If the output stage overloads at an output voltage of V' , the maximum gain is limited to a value given by $G(\delta T_A + T_R/\sqrt{n}) = V'$. The maximum error in the mean value of the recorded reading is therefore given by

$$\delta T_A/V = (\delta T_A + T_R/\sqrt{n})/V',$$

therefore

$$\delta T_A = [V/(V' - V)] T_R/\sqrt{n}.$$

In practice it is not convenient to make V' many times V , so that a static 'following' error of the same order of magnitude as the residual fluctuations of amplifier noise ($T_R/\sqrt{n}$) is to be expected. Although such a gain could be used satisfactorily under static conditions, the response to rapid changes of equivalent aerial temperature would be poor owing to the fall of gain which would result from overloading of the amplifier with a steadily increasing input from the aerial. An evaluation of the optimum value of gain requires a detailed analysis of the response of the system to various wave forms of the signal envelope, such as a step function and a continuously increasing signal ('velocity lag') but with a fixed value of V'/V , it becomes necessary to reduce the gain considerably, particularly if it is required to follow changes comparable with the heating time of the diode filament. For a response time of the order of 0.2 sec., a reduction of gain of approximately 3:1 has been found most suitable for the particular diode used, and the 'following' error will therefore be of the order of $3T_R/\sqrt{n}$.

At a frequency of 175 Mcyc./sec. $T_R \approx 3000^\circ \text{K}$, and for an input band width of 2 Mcyc./sec. and an output band width of 5 cyc./sec. the error will be about 15°K .

With input e.m.f.'s corresponding to aerial temperatures greater than T_R , the output of the amplifier is given by $G(\delta T_A + T_A/\sqrt{n})$ thus giving a following error of the order of $3T_A/\sqrt{n}$. With large signals a proportional error is therefore introduced which has a value, for the same band width constants, of about $\frac{1}{2}\%$.

(ii) *Effect of a mismatch of the aerial*

If the aerial and noise diode present unequal impedances to the amplifier input circuit, the noise originating in the input circuit will develop a different input e.m.f. in the two switch positions. Thus although a negligible loss of aerial power may occur as a result of such a mismatch, the change of amplifier noise may have the effect of displacing the effective aerial temperature by a constant increment. The apparatus will then still read changes of aerial temperature correctly, but will have a displaced zero proportional to the noise power in the first circuit of the amplifier. An accurate evaluation of this error involves a knowledge of the noise power which can be affected by a change of the shunt impedance (i.e. noise due to circuit losses and transit time but excluding the anode current shot effect) and also a knowledge of the value of impedance mismatch which gives the best noise factor. For frequencies in the

neighbourhood of 175 Mcyc./sec., the grid circuit noise (including that due to a finite transit time) is likely to be of the same order as the shot noise, and an equivalent temperature (T'_R) of 1500° K can be assumed.

For the case of a 'matched' input, the variation of the input e.m.f. to the amplifier due to grid circuit noise, as small departures from the matched condition are made, can be shown to correspond to changes of aerial temperature of the order of $T'_R(1 - 4/(1 + \gamma)^2)$, where γ is the ratio of the aerial impedance to the matched value.

For a value of γ of 1.1 and $T'_R = 1500^\circ \text{K}$, the error corresponds to a displacement of the equivalent aerial temperature by 150° K. It is therefore necessary to maintain the aerial impedance accurately equal to the impedance of the diode noise source, if absolute determinations of equivalent aerial temperatures of a few hundred degrees are required. It has been shown in § 4, however, that providing changes of equivalent aerial temperature can be determined accurately, absolute measurements to this order of accuracy are usually unnecessary since the incidence of galactic radiation makes the direct measurement of solar radiation impracticable with a simple aerial system.

(iii) *Output of diode noise source*

The system relies on a knowledge of the absolute noise output of the diode in terms of the mean plate current. This requires a knowledge of the output of the diode itself, together with the effect of the attenuators used, including any impedance transformation which these may introduce.

The noise power generated by a temperature-limited diode is proportional to the load resistance through which its anode current flows. At low frequencies this may be taken as the external load applied at the valve base, and can be accurately measured. At frequencies of 200 Mcyc./sec. and higher, the lead inductance and stray capacity of the valve structure may introduce an appreciable impedance transformation which will give rise to a proportional error in the power output. Measurements at 175 Mcyc./sec. have shown that this error is unlikely to exceed 10 % with the normal type of valve with a pressed-glass base (such as the CV 172) but at frequencies higher than 300 Mcyc./sec. serious errors may arise unless a more suitable type of valve is available. Such errors could then only be eliminated by calibration against another standard of radio-frequency power.

(iv) *Overall accuracy of the system*

Apart from the initial calibration of the diode noise source which may be necessary at the higher frequencies, the theoretical overall accuracy of the automatically balancing system described in this appendix has been shown to be of the order of $\pm(150^\circ + \frac{1}{2} \%)$, with a differential accuracy of the order of $\pm(15^\circ + \frac{1}{2} \%)$. The fluctuations at the output due to noise originating in the amplifier should be of the order of $\pm 5^\circ \text{K}$. These figures are applicable for a value of T'_R of 3000° K, and a value of n (the ratio of input/output band widths) of 4×10^6 .

(v) *Measured performance of apparatus*

Measurements carried out on the system using an amplifier having a noise factor of 11 db. ($T_R = 4000^\circ \text{K}$), with an input band width of 4 Mcyc./sec. and an output band width of 4 cyc./sec. (i.e. $n = 10^6$), gave the following results:

Fluctuation of output reading: $6.5 \pm 2^\circ \text{K}$ (the calculated values is 4°K).

Maximum following error (with gain reduction factor of 0.3): $18 \pm 2^\circ \text{K}$ for small signals, and $0.4 \pm 0.05 \%$ for large signals (the calculated figures are 13°K and 0.33%).

It may therefore be seen that the performance figures which can be achieved in practice are in good agreement with theory.

APPENDIX 2. THE DESIGN OF AERIAL SYSTEMS FOR MEASURING SOLAR RADIATION

(a) *Determination of equivalent source temperature*

It has been shown in Appendix 1 how it is possible to measure the equivalent temperature of the output of an aerial feeder in terms of the output of a diode noise source. The equivalent aerial temperature can be deduced by correcting for the loss in the aerial feeder. If this loss causes a reduction of the power by a factor β , the apparent equivalent temperature of an aerial having a true equivalent temperature T_A can be shown to be $\beta T_A + (1 - \beta) T_0$, where T_0 is the temperature of the feeder.

It was shown in Appendix 1 that the use of an attenuator (α) between diode and switch reduces the effective temperature of the diode ($T_D + T_0$) to $T_0 + \alpha T_D$.

Thus equilibrium will be attained when

$$\beta T_A + (1 - \beta) T_0 = T_0 + \alpha T_D,$$

i.e.
$$T_A = \frac{\alpha}{\beta} T_D + T_0.$$

In order to determine the equivalent temperature of a $\frac{1}{2}^\circ$ source, having measured the equivalent aerial temperature, it is necessary to know Ω , the integral over a sphere of the receptivity of the aerial system relative to the receptivity in the direction of the source. An attempt to determine Ω directly, by measuring the power gain in the direction of the source, would be liable to serious errors due to ground reflexions unless carried out with the aerial mounted at the correct angle of elevation. The measurements would involve the use of an elevated source, and owing to the practical difficulty of providing such a source, it was found more convenient to calculate Ω from the polar diagram of the aerial system.

The aerial used on 175 Mcyc./sec. consisted of an array of eight half-wave dipoles mounted $\frac{1}{2}\lambda$ in front of a reflecting screen. When such an aerial is used to observe the radiation from a $\frac{1}{2}^\circ$ source, the relation between source temperature and aerial temperature (Ω/ω) for a source situated in the maximum of the polar diagram is 6.4×10^3 . If two such aerials are used for measuring solar radiation separately from

the galactic background, the difference between maximum and minimum of the equivalent aerial temperature as the interference pattern is swept past the sun must therefore be multiplied by 3.2×10^3 in order to give the equivalent temperature of a $\frac{1}{2}^\circ$ source. If such observations are made at times other than near noon (when the sun is near the maximum of the polar diagram of each aerial in the horizontal plane),

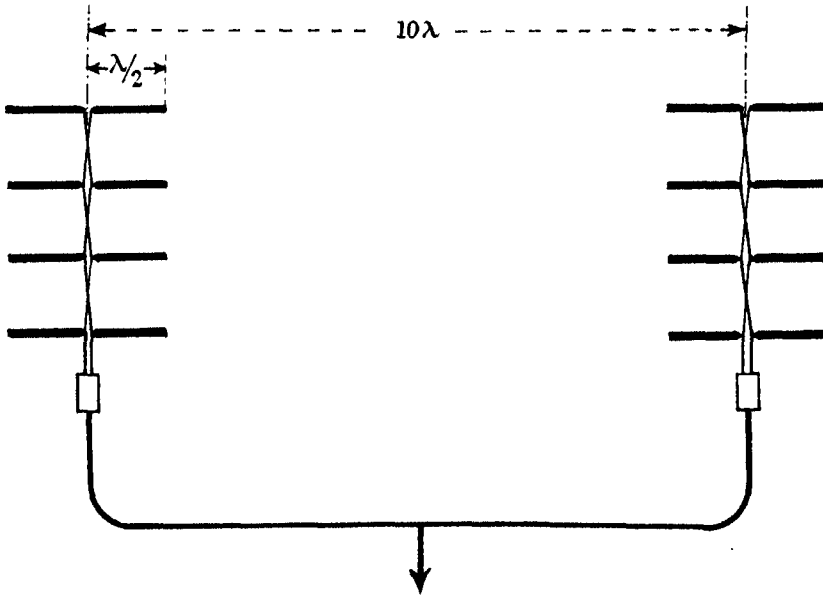


FIGURE 9. Aerial system used at 175 Mc/sec.

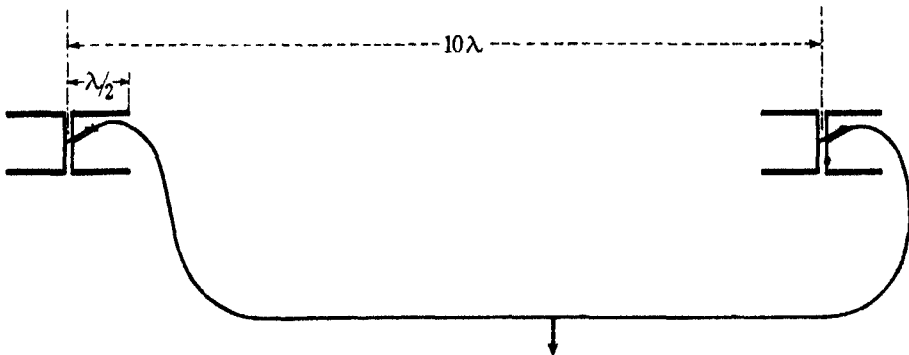


FIGURE 10. Aerial system used at 80 Mc/sec.

it is necessary to correct for the reduction in gain. Similarly, the elevation angle of the aerals must be adjusted throughout the year so that the maximum of the vertical polar diagram also coincides with the direction of the sun at midday. The errors which are likely to be introduced by such causes, and in the estimation of Ω , make it difficult to determine the equivalent temperature of a $\frac{1}{2}^\circ$ source to an accuracy of better than $\pm 10\%$.

On 80 Mcyc./sec. the larger size of the aerials necessitated a somewhat simpler arrangement, and only four half-wave elements were used in each half of the system. The feeding arrangements for the two types of aerial are shown in figures 9 and 10.

With aerials of this type, the smallest detectable temperature for a $\frac{1}{2}^\circ$ source is of the order of 10^4 °K.

(b) *The effect of mismatch of the aerial impedances on the measurement of source diameter*

It has been shown in Appendix 1 (c) that if the aerial feeder and diode noise source present unequal impedances to the amplifier input, a displacement of the zero of the record of equivalent aerial temperature can occur. Such a displacement would affect the observed maximum to minimum ratio if it were comparable with the amplitude at the minima, and would have the effect of increasing or decreasing the apparent diameter of the source. For an impedance mismatch ratio of 1:1:1, the maximum zero displacement of equivalent aerial temperature is of the order of 150° K. During the experiments described in § 7 the intensity of solar radiation was very great and even at the minima the equivalent aerial temperature was many times the maximum zero displacement. A mismatch of the impedance of the whole aerial system could not therefore produce an appreciable error in determining the source diameter.

An additional source of error may arise from asymmetry of the aerial system; any difference between the polar diagrams or impedances of the two aerials would cause unequal powers to reach the junction point of the two feeders, and would thus increase the observed minimum power. Such an effect would be interpreted as an increase of the source diameter.

The polar diagrams of the two aerials could easily be made sufficiently equal to introduce no appreciable error, but careful impedance measurement was necessary, since a mismatch ratio of 1:1:1 could give rise to a minimum power, with a point source, equal to 10 % of the maximum. With the maximum aerial spacing which could be used, the observed values of maximum to minimum ratio were of the order of 8:1.

It should be noted that any errors in the determination of source diameter which are due to unequal impedances of the two aerials, will result in an overestimate of the diameter. The final figure of 10 min. of arc, obtained during these experiments, is therefore a maximum value.

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Natural evaporation from open water, bare soil and grass

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[PLATE 3]

Two theoretical approaches to evaporation from saturated surfaces are outlined, the first being on an aerodynamic basis in which evaporation is regarded as due to turbulent transport of vapour by a process of eddy diffusion, and the second being on an energy basis in which evaporation is regarded as one of the ways of degrading incoming radiation. Neither approach is new, but a combination is suggested that eliminates the parameter measured with most difficulty—surface temperature—and provides for the first time an opportunity to make theoretical estimates of evaporation rates from standard meteorological data, estimates that can be retrospective.

Experimental work to test these theories shows that the aerodynamic approach is not adequate and an empirical expression, previously obtained in America, is a better description of evaporation from open water. The energy balance is found to be quite successful. Evaporation rates from wet bare soil and from turf with an adequate supply of water are obtained as fractions of that from open water, the fraction for turf showing a seasonal change attributed to the annual cycle of length of daylight. Finally, the experimental results are applied to data published elsewhere and it is shown that a satisfactory account can be given of open water evaporation at four widely spaced sites in America and Europe, the results for bare soil receive a reasonable check in India, and application of the results for turf shows good agreement with estimates of evaporation from catchment areas in the British Isles.

LIST OF SYMBOLS USED

x, y, z	Co-ordinate axes downwind, acrosswind and vertical.
u_s	Mean horizontal wind velocity in x direction measured at height z ; usually in miles/day.
T_s, T_a, T_d	Temperature of surface, air and dewpoint; usually ° F.
e_s, e_a, e_d	Saturation vapour pressure at above temperature; usually in mm. Hg.
h	Relative humidity = e_d/e_a .
Δ	de_a/dT_a .
ϕ	$(e_s - e_a)/(e_s - e_d)$.
α	Constant defining hydrolapse.
β	Bowen's ratio = $\gamma(T_s - T_a)/(e_s - e_d)$.

γ	Constant of wet and dry bulb hygrometer equation; in ° F and mm. Hg, $\gamma = 0.27$.
E_0, E_B, E_T	Evaporation rate from open water, bare soil and turf; usually in mm./day.
E_a	Value of E_0 obtained by putting $e_s = e_a$ in sink strength formula.
R_C	Short-wave radiation from sun and sky; usually in evaporation equivalent of mm./day.
R_A	Angot value of R_C for a completely transparent atmosphere.
r	Radiation reflexion coefficient. (Also used for runoff without any possibility of confusion.)
$m/10$	Fraction of sky covered by cloud.
n/N	Ratio of actual/possible hours of sunshine.
H	Net radiant energy available at surface.
K, S, C	Parts of H used in convective transfer to air, storage in water, conduction to surround.
$5B, 16T$	Depths to water-table (in.) and type of cover (bare, turf).
λ	Specific yield of soil.
R, D	Rainfall, drainage.
B	Beaufort wind force.

1. INTRODUCTION

Three kinds of surface are important in the return of rain to the atmosphere. For extended areas of land, they are, in order of importance: vegetation, on which plant leaves act as transpiring surfaces; bare or fallow soil, from which water evaporates at, or just below, the soil-air interface; and open water, from which evaporation takes place directly. Although the last may be of predominant importance locally, e.g. in attempting to assess the water balance of lakes and reservoirs, the chief justification of the great attention given to it (see § 2, below) is found in the opportunity it presents of providing a reproducible surface of known properties. Because of this, it is convenient to approach the problems of the dependence of evaporation from bare and cropped soil on weather conditions through a study of evaporation from open water, seeking an absolute relation between weather elements and open water evaporation, and comparative relations between losses from the soil and losses from open water exposed to the same weather.

Evaporation from bare soil involves complex soil factors as well as atmospheric conditions: transpiration studies add to these further important physical and biological features, for a plant's root system can draw on moisture throughout a considerable depth of soil, its aerial parts permit vapour transfer throughout a considerable thickness of air, and its photo-sensitive stomatal mechanism restricts this transfer, in general, to the hours of daylight. A complete survey of evaporation from bare soil and of transpiration from crops should take account of all relevant factors, but the present account will be largely restricted to consideration of the early stages that would arise after thorough wetting of the soil by rain or irrigation, when soil type, crop type and root range are of little importance.

2. THE ESTIMATION OF EVAPORATION FROM WEATHER DATA

Two requirements must be met to permit continued evaporation. There must be a supply of energy to provide the latent heat of vaporization, and there must be some mechanism for removing the vapour, i.e. there must be a sink for vapour. Analytical attacks on the problem start from one of these two points and it is convenient to consider the latter first as it has been the more popular.

(a) *Sink strength*(i) *Empirical equations*

Until recent years the approach was empirical, a hundred years' work since Dalton having produced little improvement in the form of equation he gave. In essentials it is

$$E = (e_s - e_a) f(u), \quad (1)$$

where E is the evaporation in unit time, e_s is the vapour pressure at the evaporating surface, e_a is the vapour pressure in the atmosphere above, and $f(u)$ is a function of the horizontal wind velocity. For water, e_s is known if the surface temperature is known. Of the many empirical formulae cast into this form, one due to Rohwer (1931) summarizes results of very intensive work at Fort Collins, Colorado, at 5000 ft. above sea-level. Other things being equal, Rohwer found a small variation of evaporation rates with atmospheric pressure, and reduced to conditions at sea-level, his equation for the daily rate from an open water surface 3 ft. square is

$$E = 0.40(e_s - e_a)(1 + 0.27u_0) \text{ mm./day}, \quad (2)$$

where vapour pressures are in mm. mercury, and wind speed at ground level is in m.p.h. Examining the effect of size of surface on evaporation rates, over a period of 485 days, he compared the observed values of evaporation from a large surface 86 ft. diameter with the estimates based on (2), and found the mean value of observed/estimated to be 0.77. There is some bias here, however, for the average wind speed over the whole period was only 1.50 m.p.h., and examination of the individual daily records shows that on the rare occasions of a wind speed in excess of 3 m.p.h. the correction factor is nearly unity. The ground wind velocity, u_0 , is an extrapolated value estimated from a number of readings at various heights, and if from Rohwer's u, z curve we interpolate at 2 m., the relation becomes

$$E = 0.40(e_s - e_a)(1 + 0.17u_2) \text{ mm./day}, \quad (3)$$

and except at very low wind speeds might be expected to apply to large open water surfaces.

(ii) *Aerodynamic equations*

As an alternative to this empirical treatment an aerodynamical approach has been made in recent years. A simple treatment (Penman 1940) showed that the right order of magnitude could be obtained by assuming that the main resistance to the evaporation current is provided by a thin layer of air (c. 1 to 3 mm. thick) next to the

surface, in which air movement is essentially non-turbulent, and vapour movement across which is by a process of molecular diffusion. The more formal treatment, having wider implications than the solution of evaporation problems, has considered the turbulent mixing and transport of the vapour outside this sublamina boundary layer, and it attempts to take into account the dependence of evaporation rates per unit area upon size and shape of the test area as well as upon weather elements. An account of this work is given by Brunt (1939) up to and including the work of O. G. Sutton (1934). Extension of Sutton's work by W. G. L. Sutton (1943) and Pasquill (1943) has given an expression for the *total* evaporation from a rectangular strip of length x_0 downwind and width y_0 :

$$E(x_0, y_0) = C(e_s - e'_d) u_2^{0.76} x_0^{0.88} y_0, \quad (4)$$

where C is a constant related to the absolute temperature, e'_d is the vapour pressure of the air at a height great enough to be unaffected by the evaporation, and u_2 is the wind velocity at $z = 2$ m. Although e'_d is unobservable, it has been possible to use the same general theory to express the shape of the hydrolapse, and to set $(e_s - e_d) = \alpha(e_s - e'_d)$ where e_d is the measured value at screen height, and α (≈ 0.52) is almost independent of u and x_0 . Differentiating (4), the rate of evaporation at x_0 is obtained, and, substituting numerical values appropriate to zero temperature gradient, it becomes

$$E = 0.11(e_s - e_d) u_2^{0.76} x_0^{-0.12} \text{ mm./day.} \quad (5)$$

In the open it is impossible to fix the position of the leading edge, but arbitrarily putting $x_0 = 1.6 \times 10^6$ cm. (10 miles), the evaporation rate becomes

$$E = 0.376(e_s - e_d) u_2^{0.76} \text{ mm./day,} \quad (6)$$

where e_s and e_d are in mm. mercury, and u_2 is now in miles/hr. If u_2 is measured in miles/day—a practical convenience—the rate is

$$E = 0.033(e_s - e_d) u_2^{0.76} \text{ mm./day.} \quad (6a)$$

Notes. (1) The assumption of zero temperature gradient involves the identity of e_s and e_a , where e_a is the saturation vapour pressure at the mean air temperature; $e_s - e_d$ then becomes $e_a(1 - h)$.

(2) A tenfold increase in x_0 will decrease E in the ratio $(1/10)^{0.12}$, i.e. to $1/1.3$, and the constant in (6a) will become 0.025.

(b) Energy balance

Certain simplifying assumptions are needed; where they are known to be reasonable, reliable estimates of evaporation are possible. Using as the unit of energy the amount required to evaporate 1/10 g. of water at air temperature (59 cal.) it is possible to build up the following expression for the heat budget, H , taking into account the incoming short-wave radiation from sun and sky, and the long-wave exchanges between earth and sky (Brunt 1939; equation 15, p. 136; equation 25, p. 144):

$$H = R_C(1 - \tau - \mu) - \sigma T_a^4(0.56 - 0.092 \sqrt{e_d})(1 - 0.09m), \quad (7)$$

where R_C is the measured short-wave radiation/cm.²/day,

r is the reflexion coefficient for the surface,

μ is the fraction of R_C used in photosynthesis,

σT_a^4 is the theoretical black-body radiation at T_a °K,

e_d is in mm. mercury,

and $m/10$ is the fraction of sky covered with cloud.

Using the convenient symbols of Cummings & Richardson (1927), the heat budget is used in evaporation, E , heating of the air, K , heating of the test material, S , and heating of the surroundings of the test material, C , i.e.

$$H = E + K + S + C. \quad (8)$$

Over a period of several days, and frequently over a single day, the change in the stored heat, S , is negligible compared with other changes and the same may be true of the heat conducted through the walls of the test material container. Thus, (8) can often be safely reduced to

$$H = E + K. \quad (9)$$

The transport of vapour and the transport of heat by eddy diffusion are, in essentials, controlled by the same mechanism, and apart from the differences in the molecular constants, the one is expected to be governed by $(e_s - e_d)$ where the other is governed by $(T_s - T_a)$. To a very good approximation, therefore, it is possible to write down the ratio of K/E in the form

$$K/E = \beta = \gamma(T_s - T_a)/(e_s - e_d), \quad (10)$$

where β , the ratio symbolized by Bowen (1926) as R , has the value -1 in the standard wet and dry bulb hygrometer equation, and γ is the standard constant of this equation. In °F and mm. Hg, $\gamma = 0.27$.

Thus
$$H = E(1 + \beta), \quad E = H/(1 + \beta). \quad (11)$$

Of the terms on the right-hand side of (7), the radiation term will rarely be directly measurable, but for periods of the order of a month or more it can be estimated from duration of sunshine. Angot has given tables of the total radiation to be expected if the atmosphere were perfectly transparent (Brunt (1939), p. 112), and there appears to be a general correlation between R_C/R_A and n/N in the form $R_C/R_A = a + bn/N$, where n/N is the ratio actual/possible hours of sunshine. For Virginia, U.S.A., Kimball (1914) finds $a = 0.22$, $b = 0.54$; for Canberra, Australia, Prescott (1940) finds $a = 0.25$, $b = 0.54$. At Rothamsted, monthly values over the period 1931-40 lead to $a = 0.18$, $b = 0.55$, with a suggestion of a seasonal variation. Using these latter constants we have

$$R_C = R_A(0.18 + 0.55n/N). \quad (12)$$

In terms of the maximum to be expected (R_N ; for $n = N$), equation (12) becomes

$$R_C = R_N(0.25 + 0.75n/N), \quad (12a)$$

agreeing with the form given by Angstrom for Stockholm (Brunt (1939), p. 127).

The value of μ is very small (c. 0.005) and can be neglected. The value of r will vary with season and type of surface. For water its annual mean will be about 0.06 in the British Isles; for bare soil, about 0.10; and for turf might be about 0.20 (Geiger (1927) quoting Angstrom). Note that r and β will be the only effective factors in (7) discriminating between the different types of surface.

The terms expressing the net flow of radiation to and from a cloudless sky are due to Brunt and are based on the mean values of the constants obtained in six correlations of the energy flow with mean air temperature. Sverdrup (1945) gives a diagram indicating values of the same order but with slightly greater values of $\sigma T_a^4 f(e_a)$. The uncertainty here, however, is negligible compared with that arising from the cloudiness term. It is obvious that cloud control of long-wave radiation must depend upon cloud type, and as a provisional expedient to make some allowance for this it is proposed to set $m/10 = 1 - n/N$. Equation (7) therefore reduces to

$$H = E(1 + \beta) = (1 - r) R_A(0.18 + 0.55n/N) - \sigma T_a^4(0.56 - 0.092\sqrt{e_a})(0.10 + 0.90n/N) \quad (13)$$

where $R_A(0.18 + 0.55n/N)$ is to be replaced by R_C when this is known. The parameters represented on the right-hand side of (13) are easily determined; to obtain E it is necessary to obtain β , which involves knowing the surface temperature (equation 10). The sink strength approach also involves this knowledge, and although arrangements can be made to measure it experimentally, it is desirable to eliminate it for the prediction of evaporation or for a survey of evaporation as a climatic element.

(c) Combination of sink strength and energy balance

From (1), expected to take the form of (6) or (6a), we have

$$E = (e_s - e_a) f(u). \quad (1)$$

Let E_a be the value of E obtained by putting e_a instead of e_s . Then

$$E_a = (e_a - e_a) f(u),$$

$$\text{i.e.} \quad E_a/E = 1 - (e_s - e_a)/(e_s - e_a) = 1 - \phi \text{ say.} \quad (14)$$

From (10) and (11);

$$E = H/(1 + \beta) = H/[1 + \gamma(T_s - T_a)/(e_s - e_a)].$$

If we set $T_s - T_a = (e_s - e_a)/\Delta$, where Δ is the slope of the $e : T$ curve at $T = T_a$, then

$$H/E = 1 + \gamma(e_s - e_a)/\Delta(e_s - e_a) = 1 + \gamma\phi/\Delta. \quad (15)$$

$$\text{From (14) and (15);} \quad E = (H\Delta + E_a\gamma)/(\Delta + \gamma), \quad (16)$$

$$e_s = (e_a - \phi e_a)/(1 - \phi), \quad (17)$$

i.e. E can be estimated from air conditions only, and, if required, an estimate of surface temperature can be obtained that might be useful outside evaporation studies.

In addition to the constants, readily obtainable from standard sources, the weather parameters needed are mean air temperature, mean dewpoint, mean wind velocity at a standard height and mean duration of sunshine.

3. ROTHAMSTED EXPERIMENT 1944, 1945

(a) *Experimental site*

Experiments have been carried out in the meteorological enclosure at Rothamsted, situated at about 420 ft. above O.D. in open parkland in the Chiltern Hills. The enclosure includes a brick-lined pit, 8 ft. deep and 20 ft. diameter, around which twelve cylinders were set in the soil in 1924, five of them being filled with a sandy loam from Woburn (Bedfordshire), the soil texture being uniform throughout. The cylinders are 6 ft. deep and 2 ft. 6 in. diameter and are made of cast iron lined with a $\frac{1}{2}$ in. layer of bitumen painted concrete; the bottoms have a slope down to an outlet pipe accessible from the pit. (See figure 1 and figure 7, plate 3.)

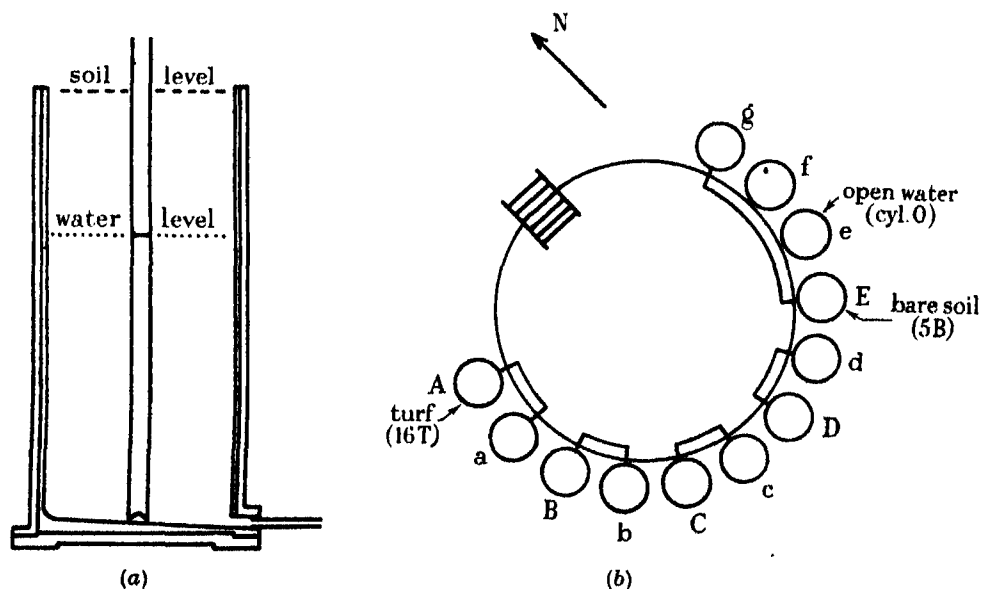


FIGURE 1. (a) Section of cylinder, and (b) plan of the pit.

The soil was left to settle and weather for 16 years so that some semblance of natural structure could be attained and by May 1940 the settlement amounted to 6 in. This was made good by a further supply of Woburn soil, experimental work was done in 1941 and 1942 and in the spring of 1944 there was a further slight topping up in preparation for the work now to be described.



FIGURE 7. The experimental site June 1944, looking north-east.

Ten cylinders were joined up in pairs at the outlets, each soil cylinder being connected to an unfilled cylinder referred to below as the 'minor', so forming a set of U tubes. Figure 1 shows the arrangement schematically, with three cylinders labelled (O, 5B and 16T). These are the main ones to be discussed and were the same in both years; changes were made in the others early in 1945. Waterproof covers were provided for the minors to prevent entry of rain and to reduce evaporation losses to negligible amounts. On A and C turves were laid in April 1944 and on D in March 1945; the other soil surfaces were kept bare.

At the outset the minors were filled with water until the soil or turf surfaces were flooded and then water was run out until the water-table had reached a pre-determined depth below the soil surface. The depths and the nature of the surface are given in table 1:

TABLE 1. DEPTHS (IN.) OF WATER-TABLE AND NATURE OF SURFACE

cylinder ...	A	B	C	D	E
1944	16 (T)	16 (B)	10 (T)	10 (B)	5 (B)
1945	16 (T)	24 (B)	24 (T)	36 (T)	5 (B)

Cylinder e was filled to near the brim and the level kept at about 1 in. below. This was the first open water standard, referred to as cylinder O. In the early summer of 1945 a tank of sheet galvanized iron, 2 ft. 6 in. diameter and 2 ft. deep was supplied by the Meteorological Office and was set up at the north end of the enclosure about 50 yd. north of the pit. A hole 1 ft. 9 in. deep was dug into which the tank fitted firmly, and the water-level was kept at or near ground level, so leaving a projecting rim of 3 in. This tank, referred to as tank MO, had the same area as the cylinder but was shallower, had a thinner and more conducting wall material, was completely surrounded by turf-covered soil whereas the other had the pit on one side, and had a higher effective rim.

Ground level round the cylinders had been raised so that soil level was the same inside and out except on one side of cylinder O where the topping up was not complete; for all the cylinders there was a big discontinuity in surface on the pit side and although the pit should have been roofed in, it was not practicable at the time and a major objection to the experimental site had to be accepted as unavoidable. Figure 7, plate 3, shows the exposure to the north-east and the disposition of some of the other components of the enclosure; in the centre, beyond the pit, is the large rain gauge (1/1000 acre) used for rainfall values employed below, and to the right of it are visible two of the bare drain gauges on which earlier Rothamsted work was based. The general exposure here is good, although the presence of the large gauges might affect local eddies with east and north-east winds. The general exposure to north-west was equally good, that to south-west a little worse, and that to south-east poorest of all due to an extended belt of trees, the nearest being about 80 yd. away.

The surround varied during the experiment. The local exterior topping up remained bare for a while, but a crop of weeds soon developed and gave a local cover nearly enough equivalent to the turf of the enclosure. By the summer of 1945 there

was a fair amount of grass in this and it was possible to cut it with a mower. Growth was very rapid during 1945 and part of the surround, too rough for a mower, got out of hand and for a while there was a stand of tall grass on the west side which may have had an adverse effect on transpiration from cylinder A (16T). In both years the field to the east was sown with mangolds giving a green cover from June until late autumn, at which time the soil surface was moist and remained moist for the remainder of the winters. The field to north and west carried an oat crop in 1944, about 1 ft. high in May, 3 ft. high throughout July and harvested in early August; the undersown clover then provided a green cover for the remainder of the season, was grazed during 1945, but grew away from the animals and a hay crop was eventually taken from it. To the south there was a pasture, kept short by grazing. Thus, except for short periods, the experimental surfaces could be reasonably described as being in the midst of an extensive area of short vegetation and as long as this transpired at maximal rate, then for so long did the experimental conditions come close to satisfying the basic assumptions from which equation (6) was derived.

(b) *Measurements and calibrations*

In addition to the normal 09.00 observations of a third-order meteorological station, supplementary measurements were made.

(i) *Temperature.* Mercury-in-steel thermographs were set up on cylinders C, D, E and O; that on D was transferred to tank MO in June 1945. The long bulbs were horizontal and were either pressed into the soil or supported in the water so that about half was below the surface and half above the surface; the water bulbs had sheaths of muslin to ensure that they were always wet all over. They were calibrated in place, and in all cases the corrected 'surface' temperature is more truly the mean temperature of the top few mm. of soil or water. To find the daily mean a smooth curve was drawn through the thermogram and a mean of six readings at 4 hr. intervals found; this was corrected from the calibration curve and the corresponding value of the saturation vapour pressure taken as the daily mean value of e_s .

Only one value of the dewpoint was obtained per day and although this was found to be adequate for long period surveys it was not always adequate for individual days, particularly where there was a pronounced change during the day. The Dunstable Branch of the Meteorological Office kindly supplied estimates of the dewpoint at 6 hr. intervals for each day and from these it was possible to see the way in which the dewpoint had changed in a given period of 24 hr. and to weight the Rothamsted values accordingly. Obtaining a reliable daily mean value of the dewpoint remains one of the main experimental problems to be solved.

The mean air temperature is never of first order of importance and it has been sufficient to take the conventional mean of maximum and minimum for this parameter.

(ii) *Wind.* A three-cup anemometer was set up at 2 m. in the south-west corner of the enclosure in 1944, and was moved to the middle of the enclosure early in 1945 so as to be about half-way between the pit and the new MO tank. The scale reading

was read once daily, and in view of this it was an obvious convenience to use miles/day as the unit of wind velocity (equation (6a); figures 2 and 3). The instrument was calibrated in December 1944 in terms of a similar instrument with smaller cups, with which a calibration curve was supplied. The curve was non-linear at low speeds and calibration of the experimental instrument is consequently uncertain in this region: table 2 shows the result:

TABLE 2. CALIBRATION OF ANEMOMETER (MILES/DAY)

observed	0	30	60	90	120	150	210	270
corrected	38	50	78	106	133	161	215	272

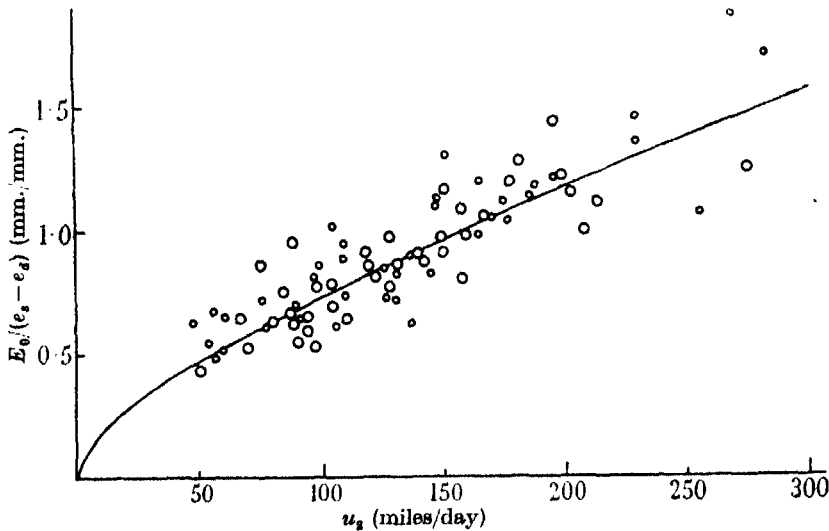


FIGURE 2. Daily evaporation per unit partial pressure difference for open water surface (cylinder O). The curve is: $E_0/(e_s - e_d) = 0.033 u_s^{0.68}$, $\square$ 1944, $\circ$ 1945.

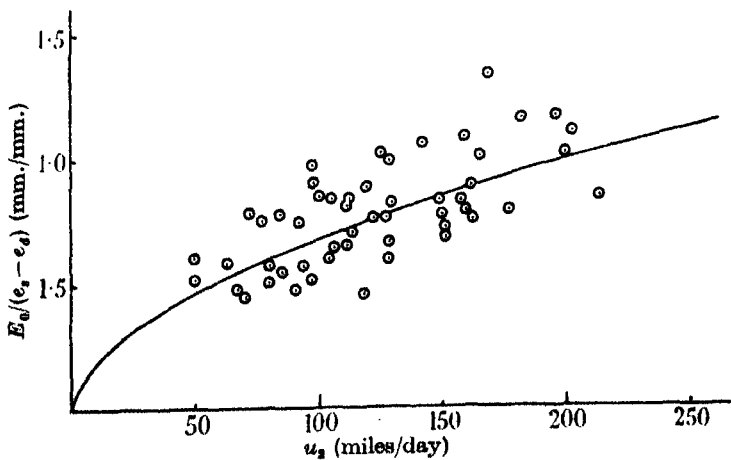


FIGURE 3. Daily evaporation per unit partial pressure difference for open water surface (tank MO). The curve is: $E_0/(e_s - e_d) = 0.065 u_s^{0.54}$.

A Dines wind recorder on the laboratory roof, about $\frac{1}{2}$ mile away, was used to estimate direction and variation of wind speed during the day, where necessary.

(iii) *Radiation*. A continuous record of radiation intensity on a horizontal surface was obtained each day, the total area under the trace measured by planimeter and the figure so obtained converted to the equivalent number of mm. of water that the total energy would evaporate at air temperature.

The duration of sunshine was obtained from a Campbell-Stokes recorder.

(iv) *Evaporation*. Daily measurements were made of the depth of the water-levels below arbitrary zeroes.

Cylinders A, B, C and D. A rigid cradle was built into the top of the minor into which could be fitted a framework carrying a screw ending in a sharp pointed dipstick. The screw carried a scale that moved past a fixed index mark and readings could be made to better than $\frac{1}{8}$ mm. except on very windy days.

Cylinders E and O. Measurements here were somewhat cruder. A solid straight edge was placed across the top of the minor in a marked position and, by means of a guide, a pointed rule was slid down until it just touched the water surface. With care, readings could be reproduced to within about $\frac{1}{8}$ mm., and in the major part of the experiment this was adequate accuracy.

Tank MO. A hook gauge reading to $\frac{1}{100}$ in. was used.

Changes in level are due to evaporation or rainfall, both being excluded from the minors. A fall in level takes place in both arms of the U system when evaporation occurs, so that for a change in minor level of δz , the total evaporation is greater, and may be set equal to $\delta z(1 + \lambda)$, where λ is the specific yield of the soil with water-table at z cm. below the surface. If, over a period, the measured rainfall is R , then the total evaporation is given by

$$E = \delta z(1 + \lambda) + R. \quad (18)$$

As λ is a function of z , measurements were made to give the values in table 3.

TABLE 3. SPECIFIC YIELD OF SOIL

depth of water-table (in.)	5	10	16	24	36
specific yield, λ (cm./cm.)	0.02	0.04	0.10	0.13	0.13

4. RESULTS FOR INDIVIDUAL DAYS

(a) *Open water: sink strength*

Equation (6a) was tested by plotting $E_0/(e_s - e_d)$ against u_s . Figure 2 shows the result for cylinder O with the 1944 and 1945 data distinguished, figure 3 shows the result for tank MO from mid-June 1945, and in figure 4 are given values of $\Sigma E_0/\Sigma(e_s - e_d)$ for wind speed ranges sufficiently wide to include at least four observations in the summations. The data represented in these figures have been selected as follows: (i) rain days have been excluded as there is some uncertainty about the uniformity of rainfall distribution over the site; on such a day the fall in level is made up of evaporation minus rainfall. (ii) For cylinder O, only those days have

been used in which $E_0 > 2.5$ mm. and $(e_s - e_d) > 2.5$ mm.; for tank MO, to increase the number of available results, the limits were lowered to 2.0 mm. The experimental errors tend to be absolute and the uncertainty in the ratio increases greatly as E_0 and Δe become very small.

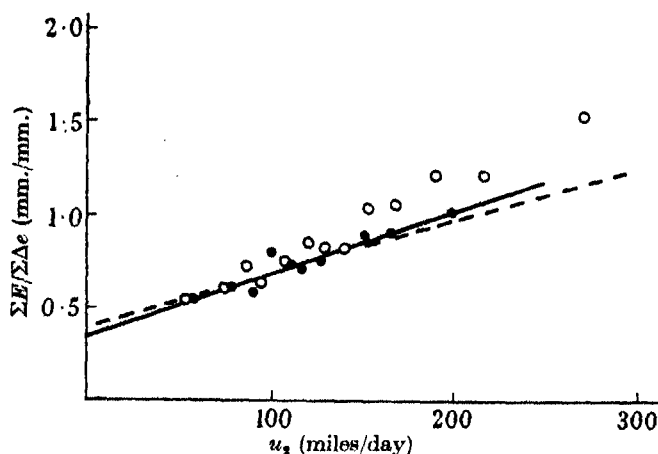


FIGURE 4. Mean daily evaporation per unit partial pressure difference for open water (groups of days having approximately the same average wind speed). The continuous line is: $E_0/(e_s - e_d) = 0.35(1 + 9.8 \times 10^{-3} u_2)$. O cylinder O; —●— tank MO; --- Rohwer.

The scatter in figures 2 and 3, although not very much worse than that obtained by other workers doing indoor experiments, is considerable. A number of obvious contributory factors have been examined and shown to be of slight effect: dryness of the surround, wind distribution during the day, height of rim and season of the year. The main sources are undoubtedly the meteorological observations themselves; in increasing order of importance they are: dewpoint and surface temperature determinations and wind velocity measurements. Concentrating on the last, it is doubtful whether a measurement at a single height and the assumption of zero velocity at ground level are sufficient to define the wind velocity profile even over a smooth surface; they cannot be expected to take account of the local turbulence introduced by many obstructions and surface irregularities. These will vary with wind direction, and an analysis of the cylinder O results showed that all high values of $E/\Delta e$ at high u_2 were for days with north-east winds, i.e. days in which the local exposure would be most conducive to extra turbulence. It seems, therefore, that in spite of their greater scatter, the tank MO results are probably a better guide to a general law than the cylinder O results, and this is supported by the comparison (figure 4) with Rohwer's results. (Because of the scatter it is probable that the mean curves do not differ significantly.) The mean curves show that there is a linear relationship between $E/(e_s - e_d)$ and u_2 , but for comparison with the theoretical form two curves could be fitted: (i) through the overall mean value of $E/\Delta e$ and of u_2 , a curve $E/\Delta e = bu_2^{0.76}$ (cf. equation 8a) and, (ii) through the two general means obtained from the groups

of points lying to the left and right of the overall mean, a curve $E/\Delta e = au_2^n$. The results, in decreasing order of efficiency, are given in table 4.

TABLE 4. VALUES OF $f(u)$ IN $E_0 = (e_s - e_d)f(u)$

	cylinder O	tank MO	Rohwer*
best	$0.30(1 + 14.2 \times 10^{-3}u_2)$	$0.35(1 + 9.8 \times 10^{-3}u_2)$	$0.40(1 + 7.1 \times 10^{-3}u_2)$
good	$0.033u_2^{0.66}$	$0.065u_2^{0.54}$	—
fair	$0.021u_2^{0.76}$	$0.019u_2^{0.76}$	—

The curves drawn in figures 2 and 3 are the 'good' curves, wind velocities being in miles per day.

From the above, it is concluded that: (i) the best form of (1) for practical use is

$$E_0 = 0.35(1 + 9.8 \times 10^{-3}u_2)(e_s - e_d) \text{ mm./day, } u_2 \text{ in m.p.d.;} \quad (19)$$

(ii) for analysis, demanding a curve passing through the origin, the power of the wind velocity is much nearer $\frac{1}{2}$ than $\frac{3}{2}$; (iii) if the form of equation (6a) is to be maintained, the constant is to be reduced from 0.033 to about 0.020, a result that may be due to inaccurate assumptions about the distance away of the hypothetical 'leading edge', may be due to the departure from zero temperature gradient, or may be due to an inaccurate value of α in specifying the shape of the hydro-lapse.

(b) Open water: energy balance

The initial objective in this approach was an application to extended periods in which the assumptions made in reducing (8) to (9) would be reasonable; the main discussion will be of this aspect and appears below, but in view of its success it seemed worth while extending the application to individual days. An estimate of E_{MO} , based on energy, was obtained for most days between mid-June and the end of September 1945 and results are shown in figure 5 and table 5. The latter includes a representative sample of the data of the figure, the choice being made at roughly 6-day intervals with an attempt to give reasonable ranges of wind velocities and sunshine conditions, and affords a comparison of the estimates based on energy balance and sink strength (equation 19) with each other and with the observed values of daily evaporation. The values of $(e_s - e_d)$ range from 1.10 to 7.40 mm., those of σT^4 from 13.6 to 14.8, those of $(0.56 - 0.092\sqrt{e_d})$ from 0.30 to 0.26, the product of the last two functions tending to be constant, and those of $(0.10 + 0.90n/N)$ from 0.10 to 0.70. From the last, it will be seen that the most important term in the back radiation is the cloudiness factor—the least certain of any. Although they could be deduced from other columns, values of β are given. The figure is extremely encouraging. With the table it shows that the energy balance estimate is too big in mid-summer but improves later in the year. The change in the reflexion coefficient (here taken as constant throughout) would act in the opposite sense, and apart from

* Wing-Cdr Frost, in a private communication, has stated that observations at Poona, India, which were reduced to the form $E/\Delta e = au^{0.28}$ by the experimenters can be equally well fitted by

$$E = 0.40(1 + 7.3 \times 10^{-3}u_2)(e_s - e_d) \text{ mm./day.}$$

This is almost indistinguishable from the Rohwer equation.

any deficiencies in (13) itself it is probable that the main cause of the over-estimate is the warming of the bottom of the tank to a higher temperature than the outside soil so producing a positive value of the factor C in (8). The neglect of C in (9), therefore, leads to an over-estimate of H and hence of E .

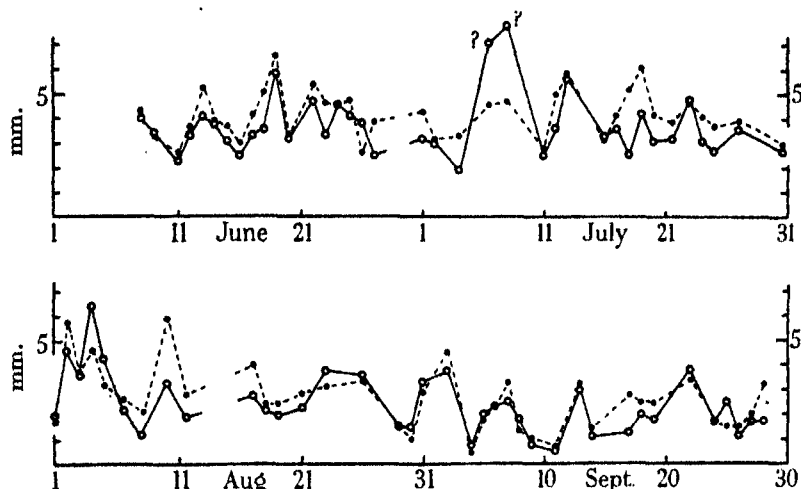


FIGURE 5. Comparison of the observed daily evaporation from open water (tank MO) and estimates based on the energy balance. —○— observed; —●— energy balance estimate. Year 1945.

TABLE 5. ENERGY BALANCE ESTIMATE FOR TANK MO FOR INDIVIDUAL DAYS, COMPARED WITH THE OBSERVED VALUE AND THE SINK STRENGTH ESTIMATE (EQUATION 19)

date 1945	u_2 (m.p.d.)	$0.95R_0$ (mm./day)	H (mm./day)	β	evaporation (mm./day)		
					estimates	observed	
					$H/(1+\beta)$	$\Delta cf(u)$	E_{MO}
June 11	149	4.36	3.64	0.37	2.6	2.4	2.3
16	80	5.62	4.52	0.48	3.0	2.7	2.5
22	92	8.28	5.58	0.03	5.4	4.2	4.7
27	118	7.19	4.82	0.35	3.9	4.1	2.5
July 1	197	7.16	5.01	0.16	4.3	4.7	3.2
8	96	8.49	5.98	0.28	4.7	4.8	7.8?
12	50	8.19	5.80	0.15	5.0	3.1	3.6
17	111	6.45	4.78	0.15	4.2	3.2	3.6
23	128	9.09	5.76	0.23	4.7	5.7	4.8
30-31	129	3.72	2.78	-0.07	3.0	2.6	2.7
Aug. 3	67	7.58	4.11	0.12	3.6	4.3	3.6
8	80	3.65	2.67	0.25	2.1	1.4	1.2
17	122	5.65	3.76	-0.07	4.0	2.8	2.8
23	182	5.00	3.43	0.06	3.2	3.2	3.8
26	63	7.23	3.90	0.17	3.4	3.4	3.6
Sept. 2	196	5.40	3.70	-0.18	4.5	3.3	3.8
8	128	1.90	1.53	0.15	1.3	1.4	1.8
9	50	1.43	1.07	0.04	1.0	0.8	0.8
14	133	1.72	1.36	-0.02	1.4	0.9	1.1
22	169	4.52	2.34	-0.31	3.4	2.3	3.8
27	146	3.17	1.63	-0.17	2.0	2.3	1.7

From the table the sink strength estimates based on the fitted curve appear to be a little better than the energy balance estimates. The correlation coefficients between observed and estimated values are about 0.80 in each case, and when it is remembered that the fitting has reduced the sink strength estimate to about 60 % of its theoretical value it is apparent that on the basis of the original predictions the energy balance estimate is the better. The two estimates agree on 8 July when the observed value was extremely high and was queried at the time of observation. In open country there are several causes of spurious high readings; rabbits and birds appreciate an open pool on a hot day and although the enclosure was refitted with wire netting for this experiment it is impracticable to take measures to ensure 100 % freedom from intrusion. Leaks are usually unidirectional and although a big leak is easily noticed, a small one, particularly if variable, could easily be overlooked. Replication is the only safe control here, and the close agreement of the sink strength results for cylinder O and tank MO is regarded as confirmation of the general water-tightness of both containers.

(c) Evaporation on individual days (other surfaces)

No detailed analysis has been attempted, for two reasons. With water-tables at some distance below the surface there is always some drying out of the soil above the water-table that does not affect the water-table, so that on rain-free days the movement of the water-table does not represent all the evaporation taking place. On a rain day, no rise in water-table will occur until this accumulated deficit of moisture has been made up and on such days the estimate of evaporation based on water-table movement and rainfall will be excessive.

The second reason is that changes in soil temperature from day to day produce changes in the surface tension of the water held in the soil above the water-table and slight water movements take place accordingly. During dry periods the movements of the water-table in cylinder 24 B were due almost entirely to temperature changes, and evaporation was negligible by comparison.

Over an extended period the effect of temperature changes under the saturated surfaces is negligible; if the period is chosen so that its beginning and end are marked by a rise in water-table due to rain then one can be sure that the soil moisture content above the water-table is the same at beginning and end, and (18) can be applied with confidence. Such periods have been termed 'natural periods' (Penman & Schofield 1941) and are the basis of the ensuing discussion.

5. EVAPORATION IN NATURAL PERIODS

(a) General

The main discussion will be confined to the open water surfaces, the bare soil with water-table at 5 in. and the turf with water-table at 16 in., but it will be useful to give a brief account of the performance of other cylinders. The bare soil cylinders with water-tables at 10, 16 and 24 in. failed to satisfy the condition of continuous

saturation at the surface; the first showed signs of drying during extended periods of rainfree weather and the other two were almost continuously dry except for a day or two after rain. Under turf, the water-table at 10 in. was probably too high for the proper development of the plant, and both growth and transpiration were slightly less than for cylinder 16T; the 1945 results showed transpiration to be about the same for cylinders 16T and 24T, although the crop yield was greater on the latter; the turf over the deepest water-table (cylinder 36T) failed to establish itself with the same luxuriance as the others and little of any value has yet emerged from the results.

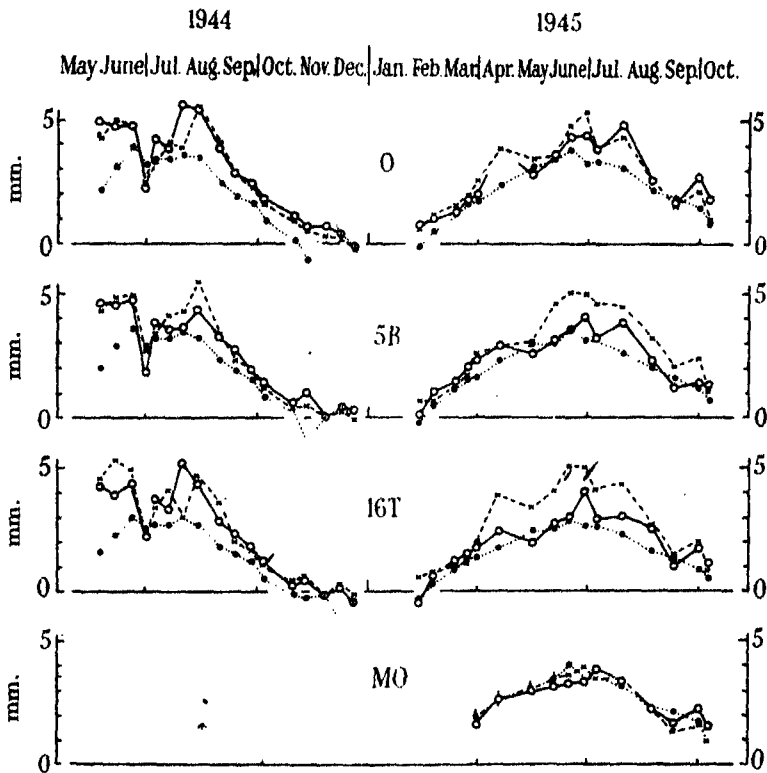


FIGURE 6. Mean daily evaporation in natural periods for surfaces with non-limiting water supply. (Open-water: O and MO. Bare soil with water-table at 5 in.: 5B. Turfed soil with water-table at 16 in.: 16T.) —○— Observed values. Estimates: --x-- sink strength, ..●.. energy balance and ● combined.

The results of 18 months for cylinders O, 5B, 16T and tank MO are summarized in figure 6, and with a few supplementary notes the figure should be almost self-explanatory. Apart from the large winter gap, when snow and ice prevented readings from being obtained, there are one or two minor gaps of a few days when records were unobtainable. The lines drawn have no significance other than helping the eye to follow seasonal changes.

The sink strength estimates are based on the mean wind velocity for the period, and the mean values of T_s and T_a from which e_s and e_a were derived. For cylinders O, 5B and 16T the linear expression derived for cylinder O was used (table 4, column 1); for tank MO the corresponding equation (19) was used.

The radiation estimates are based on (13) and (9), using reflexion coefficients of 0.05, 0.10 and 0.20 for open water, bare soil and turf respectively; for cylinder O and tank MO, therefore, the value of H was the same, but the values of β were not necessarily the same, depending upon the values of the surface temperatures.

As the surface temperature of tank MO was not measured until mid-June 1945, the combined estimate (equation 16) was made for the preceding natural periods.

(b) *Comments and conclusions*

(i) For cylinder O the sink strength estimate is a reasonably good fit throughout, suggesting that in selecting results for figure 2 there has been no undue bias.

(ii) For cylinders 5B and 16T the sink strength estimate is good in 1944 but too big in 1945. It is difficult to interpret the turf results as the thermometer bulb was usually covered by growing grass of varying length; perhaps one ought to be surprised at such an exposure combined with a formula based on open water leading to results so near observation. In the case of the bare soil, a reasonable explanation is available. During the summers, and particularly in 1945, a tough wiry weed established itself on the surface and by its mere physical presence probably slowed up evaporation by decreasing wind speed over the surface. As a result of this a little more heat would be available for warming the surface, i.e. T_s , and hence e_s and $(e_s - e_a)$, would increase, so leading to an increased estimate as a result of a decreased observed evaporation.

(iii) For cylinders O, 5B and 16T the radiation estimates are almost invariably too low. In some of the winter periods the value of β reached very uncertain values near -1 and the derived values of $H/(1+\beta)$ were absurd. These values are not plotted.

(iv) For tank MO both estimates are reasonably good and table 5 and figure 5 above may be regarded as giving the fine structure of some of the results shown in figure 6.

(v) Comparison of the results for cylinder O and tank MO so far quoted seem, superficially, to be in conflict; the same sink strength formula fits both whereas the radiation estimates fit the tank results only. The evaporation from the tank was usually about 25 % less than that from the cylinder (table 6 below), but the surface temperature was correspondingly lower, leading to the near agreement of table 5. It is suggested that the increased evaporation from cylinder O was due to the greater surface temperature, i.e. to an extra supply of energy being available to it that was not available for the tank, and that the exclusion of this additional energy supply from the energy balance for cylinder O led to the noted underestimates of evaporation on this basis. Whereas tank MO had an all-soil surround, O and the other cylinders had a hollow on one side. The air in this would warm up during the day to tem-

peratures much in excess of the soil or water in the cylinders at the same depth, leading to an inflow of heat, i.e. to a negative value of C in (8), at least for midsummer months.

It is reasonable to assume that the effect would be the same order for all cylinders, i.e. that *relative* values of evaporation from the three kinds of saturated surfaces would not be materially affected and that one of the major aims of the experiment has not been upset by the deficiency of the experimental site.

6. CONCLUSIONS FROM RESULTS OF PRECEDING PARAGRAPHS

It is convenient to interpolate a short set of conclusions based on the study of daily and periodic evaporation. Without repeating the reservations already made concerning experimental accuracy and theoretical adequacy, we have:

(a) A sink strength formula has been obtained that agrees closely with the results of intensive work by Rohwer, and is substantially the same for two open water surfaces having different environments.

(b) An energy balance has led to close agreement with observed values for one of these surfaces in which the conditions most nearly satisfy the basic assumptions made in striking the balance.

(c) The discrepancy for the other surface is of a kind that can reasonably be applicable to all the cylinders similarly exposed, so that relative values of evaporation rates may be deduced.

7. RESULTS (CONTINUED): RELATIVE EVAPORATION RATES

Table 6 shows the seasonal variation in evaporation from cylinder O, expressed in *in./day*, and the relative rates for bare and turfed soil, the natural periods being grouped roughly in calendar months. For 1945 the mean daily rates for tank MO are included. The bare soil cylinder was set up for a new experiment in December 1945 involving destruction of the surface.

Natural surfaces that are bare, such as arable land before a crop is established, will rarely remain moist in summer when weeds can grow, and will, under ordinary cultivation, rarely grow weeds in winter when the soil will remain moist. It is, therefore, permissible to select results from the preceding table and to state that the evaporation rate from a freshly wetted bare soil will be about 90% of that from an open water surface exposed to the same weather. This is in agreement with the results of indoor experiments (Penman 1941) and other outdoor work (e.g. White 1932).

It is not so easy to reach a firm decision about the grass surface. Assuming, for simplicity, that the leaf temperature is always the same as that of the open water surface, the ratio E_T/E_0 will depend upon the length of daylight (N hr.), and the difference between the minimum surface temperature and the dewpoint. If this difference is large compared with the diurnal temperature change, the value of E_T/E_0 will be of the order of $N/24$, i.e. will range from about 0.70 in summer, to about 0.30 in winter at Rothamsted. As the excess of minimum over dewpoint

temperature decreases, both these extreme ratios increase, and when the difference is zero they will be of the order 0.95 and 0.58 respectively, with a value of about 0.83 at the equinoxes (assuming a sinusoidal variation of diurnal temperature change). When the dewpoint temperature is greater than the surface minimum, conditions are more complicated, as condensation will take place on both kinds of surface, and until the dew is evaporated both will behave as open water surfaces whatever the light conditions. Under these conditions the relative evaporations over a whole day will approach equality, although the absolute amounts will tend to be small.

TABLE 6. SEASONAL VARIATION IN RELATIVE EVAPORATION

period 1944	E_0 (in./day)	E_B/E_0	E_T/E_0	period 1945	E_0 (in./day)	E_B/E_0	E_T/E_0	E_{M0} (in./day)
Feb.	—	—	—	8 Feb.—4 Mar.	0.04	0.78	0.31	—
Mar.	—	—	—	5 Mar.—7 April	0.06	1.10	0.86	0.06
April	—	—	—	8–30 April	0.10?	1.05?	0.92?	0.10
9 May–1 June	0.18	0.91	0.83	4–25 May	0.11	0.89	0.69	0.11
2–28 June	0.19	0.98	0.88	28 May–9 June				
29 June–4 Aug.	0.16	0.82	0.89	10–22 June	0.16	0.83	0.72	0.12
5 Aug.—2 Sept.	0.19	0.81	0.78	23 June–2 July				
5–30 Sept.	0.10	0.91	0.79	3–12 July	0.17	0.84	0.71	0.14
1–10 Oct.	0.05	0.65	0.48	16 July–8 Aug.				
20 Oct.—6 Nov.	0.03	0.54	0.0	12 Aug.—2 Sept.	0.11	0.87	0.96	0.08
7–13 Nov.	0.03	0.54	0.0	6–15 Sept.	0.09	0.61	0.61	0.07
20–30 Nov.	0.01	0.8	–0.4	16–24 Sept.				
1–22 Dec.	0.01	0.8	–0.4	25 Sept.—22 Oct.	0.07	0.70	0.64	0.06
				1–28 Nov.	0.03	0.7?	0.6	0.02
				29 Nov.—22 Dec.	0.05	—	–0.0	0.05

The simple initial assumption is not likely to be realized in practice, and both mean surface temperature and its daily amplitude will be important. In winter, when the important temperature differences are likely to be small and unequal there may be more condensation on one surface than another and so negative ratios might be obtained (December 1944 and 1945).

It is clear that a more detailed study of this part of the problem is needed, and at the moment only a limited generalization can be made with the reservation that it may apply to the Rothamsted site and the years 1944–45 only. Using the *totals*, for midsummer periods (May–August inclusive) the ratio is 0.81; for equinoctial periods (March–April, September–October) it is 0.72; for midwinter the results are too few and too erratic to attempt expression of a ratio. We can, however, get an indication of the order of magnitude from another source. At Fleam Dyke, Cambridge, two drain gauges, one bare and the other turfed, are maintained side by side. Over winter months, when the summer drying has been made good in both gauges, E_B is greater than E_T . For the months December–March inclusive, in the years 1939–40 to 1942–43, the totals were:

$$\Sigma E_B = 10.5 \text{ in.}, \quad \Sigma E_T = 7.6 \text{ in.} \quad \text{i.e.} \quad E_T/E_B = 0.725$$

(data kindly supplied by Mr Porteous, Engineer-in-charge, Cambridge University and Town Waterworks Co.). Putting $E_B/E_T = 0.90$, then $E_T/E_0 = 0.65$, and as the March transpiration would be greater than that in November, the midwinter ratio would be smaller. To a satisfactory degree of accuracy it may be rounded off to 0.60.

8. CONCLUSIONS FROM RESULTS OF SEASONAL VARIATION IN RELATIVE EVAPORATION

(a) The evaporation rate from continuously wet bare soil is 0.9 times that from an open water surface exposed to the same weather conditions in all seasons.

(b) The corresponding relative evaporation rate from turf with a plentiful water supply varies with season of the year. Provisional values of E_T/E_0 for southern England are:

Midwinter (November–February)	0.6
Spring and autumn (March–April, September–October)	0.7
Midsummer (May–August)	0.8
Whole year	0.75

(c) The discrepancy between cylinder O and tank MO is greatest in midsummer when the effect of extra heat flow through the walls of cylinder O is likely to be most important.

9. TESTS ON OTHER DATA

(a) Data required and methods of using them

Before the conclusions of § 8 can be applied to soil surfaces it is necessary to estimate the evaporation that would take place from an open water surface exposed to the same weather. To avoid reference back, the requirements are repeated: (i) for the sink strength estimate it is necessary to know the mean surface temperature, the mean dewpoint temperature and the mean wind velocity. Then

$$E_0 = 0.35(1 + 9.8 \times 10^{-3}u_s)(e_s - e_d) \text{ mm./day;} \quad (19)$$

(ii) for the energy balance estimate the requirements are: mean daily short-wave radiation (or mean daily duration of sunshine), mean daily cloudiness (or mean daily duration of sunshine), mean air temperature, mean dewpoint temperature, and mean surface temperature. Then

$$E_0 = H/(1 + \beta) \text{ mm./day,} \quad (11)$$

$$\left. \begin{array}{l} \text{where} \quad H = R_C(1 - r) - \sigma T_a^4(0.56 - 0.092\sqrt{e_d})(0.10 + 0.90n/N) \\ \text{and} \quad R_C \div R_A(0.18 + 0.55n/N); \end{array} \right\} \quad (13)$$

(iii) for the combined estimate there must be known, mean air temperature, mean dewpoint temperature, mean wind velocity, and mean daily duration of sunshine. Then

$$E_0 = (H\Delta + 0.27E_a)/(\Delta + 0.27) \text{ mm./day,} \quad (16)$$

where H is given by (13) above, and

$$E_a = 0.35(1 + 9.8 \times 10^{-3}u_2)(e_a - e_d) \quad (\text{cf. (19)}).$$

The values of N and R_A will vary with latitude and season, but are readily obtainable from standard sources. The value of r has a similar double variance but it will probably be sufficiently accurate to use a constant value of 0.05.

For general use, where E_0 has not been directly measured, the third method is most useful, and as the dependence on wind speed is not very critical, a Beaufort wind force can be substituted for u_2 so giving an opportunity of making an evaporation estimate from the data of a weather map. To convert the sink strength formula it is sufficient to use the 'good' expression for cylinder O (table 4) combined with two standard conversion factors:

$$E_0 = 0.033u_2^{0.68}(e_s - e_d), \quad u_2 \text{ in miles/day;}$$

$$u_2 = 0.78u_{10};$$

$$u_{10} = 1.87B^{\frac{1}{4}} \times 24, \quad u_{10} \text{ in miles/day;}$$

$$\begin{aligned} \text{i.e.} \quad E_0 &= 0.033[0.78 \times 24 \times 1.87B^{\frac{1}{4}}]^{0.68}(e_s - e_d); \\ &= 0.37B^{1.02}(e_s - e_d) \text{ mm./day.} \end{aligned}$$

The coarseness of the Beaufort estimates of wind force suggests that this may safely be reduced to

$$E_0 = 0.37B(e_s - e_d) \text{ mm./day,} \quad (20)$$

giving

$$E_a = 0.37B(e_a - e_d) \text{ mm./day}$$

for use in (16).

Although evaporation data exist for many sites over long periods of time there are not many sets that have sufficient contemporary meteorological data alongside to enable a comparison of observed and predicted evaporation to be made. The few cases discussed below have been chosen to give a fairly wide variety of sites and types of surface.

(b) Open water

(i) Fitzgerald (1886). Pans were floated in the middle of an 85 acre reservoir at *Chestnut Hill, Boston, Mass.* Table 7 gives results for a pan 10 ft. diameter and 10 ft. deep, filled to within 3 in., and sunk to within 6 in. of the top. The anemometer was at 30.5 ft. above the surface. Values of E_0 , u , T_s , T_a and h were measured on 8 days between June and October 1885. Using (19) the following results are obtained, E_{10} representing the estimates.

TABLE 7. DAILY EVAPORATION AT BOSTON, U.S.A.

day	...	1	2	3	4	5	6	7	8
u_2 (m.p.d.)		223	135	116	150	127	75	51	129
$(e_s - e_d)$ (mm.)		10.4	7.6	7.8	7.7	10.0	8.0	6.3	2.5
E_{10} (mm./day)		11.6	6.2	5.8	6.7	7.8	4.9	3.3	2.0
E_0 (mm./day)		10.7	6.8	6.1	6.6	7.1	7.1	4.1	2.5

(ii) Visentini (1936). A pan was floated in the reservoir at *Molato, Italy*, with an anemometer on the dam. Values of T_s , T_a , u and h are given. In the absence of information it is assumed that the anemometer height was 2 m. and the calibration the same as for the Rothamsted anemometer.

TABLE 8. MEAN DAILY EVAPORATION AT MOLATO, ITALY

	1934	...	Aug.	Sept.	Oct.	Nov.	Dec.
u (m.p.d.)			67	48	44	82	77
$(e_s - e_a)$ (mm.)			8.2	6.85	5.8	3.2	1.95
E_{19} (mm./day)			4.8	3.5	2.9	2.1	1.2
E_0 (mm./day)			5.1	3.9	4.1	2.3	1.3

	1935	...	Mar.	Apr.	May	June	July	Aug.	Sept.
u (m.p.d.)			106	96	99	87	91	70	72
$(e_s - e_a)$ (mm.)			3.0	5.25	3.9	8.2	8.5	6.3	5.4
E_{19} (mm./day)			2.1	3.6	2.7	5.4	5.7	3.9	3.3
E_0 (mm./day)			1.8	2.7	3.0	6.2	7.9	5.7	4.3

(iii) Davydov (1936). Measurements were made on *Sevan Lake, Soviet Armenia* (no details). Values of $(e_s - e_a)$ between lake surface and 10 cm. above, and of wind velocity at 9 m. are given. Results are means for 1927-30:

TABLE 9. MEAN DAILY EVAPORATION AT SEVAN LAKE, SOVIET ARMENIA

	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
u_2 (m.p.d.)	136	106	123	157	119	144	140	153	183
$(e_s - e_a)$ (mm.)	0.1	0.0	1.5	2.3	3.9	4.7	4.9	3.8	3.3
E_{19} (mm./day)	0.1	0.0	1.2	2.0	3.0	4.0	4.1	3.3	3.2
E_0 (mm./day)	0.4	0.2	1.2	2.1	3.4	4.5	4.1	3.6	2.9

(iv) Ray (1931). Monthly means for a standard U.S. Weather Bureau evaporation pan are given for 1917-30 for *San Juan, Puerto Rico*, together with u_0 , T_a , mean saturation deficit and mean hours of sunshine. For speed of computation a 12 hr. day has been assumed for the whole year. As results are given in in./month and $(e_s - e_a)$ in inches of mercury, the same form is kept in table 10:

TABLE 10. MEAN MONTHLY EVAPORATION AT SAN JUAN, PUERTO RICO

	Jan.	Feb.	Mar.	Apr.	May	June
E_a (in./month)	5.35	4.75	7.3	7.2	7.6	7.4
H (in./month)	3.8	5.15	6.1	7.0	7.05	7.7
E_{18} (in./month)	4.25	5.05	6.4	7.05	7.2	7.65
E_0 (in./month)	5.55	5.55	7.6	7.85	7.75	7.45

	July	Aug.	Sept.	Oct.	Nov.	Dec.
E_a (in./month)	8.55	8.15	6.05	5.0	4.8	5.75
H (in./month)	7.1	7.55	6.4	5.3	4.3	3.8
E_{18} (in./month)	7.55	7.7	7.3	5.2	4.45	4.3
E_0 (in./month)	8.15	8.05	6.6	5.85	5.1	5.45

(c) *Bare soil*

There are few records available and information about related weather is even more rare. By the courtesy of the Indian authorities, the rainfall, drainage and other weather records for Pusa have been made available from 1907 to 1934. Pusa lies in the monsoon region of Asia, at latitude 26° N. in the Ganges basin, and in most years it is a fairly reasonable assumption that once the monsoon has broken, bare soil will remain moist for most of the monsoon period.

In 1906 four drain gauges were constructed, each $1/1000$ acre in area, without disturbing the soil, two being 3 ft. deep and two 6 ft. deep. One at each depth was kept bare and the other pair cropped, and daily records of rainfall and drainage for months in which at least one gauge ran are available from 1907-34. The crop carried by gauges II (6 ft.) and IV (3 ft.) during the monsoon period was either maize (1907-15) or sunn hemp (1916-34), sowing taking place in June each year. Both are tall plants (8 ft. and 6 ft. high), and, standing well above the turf surround, they would be better ventilated, intercept more radiation and expose a larger transpiring surface to the air than a patch of the same size in the middle of a large field. Transpiration would be abnormally great, and the evidence of the cropped gauges is to be rejected on the ground that the same surface was not typical of its environment.

The records were separated into natural periods in which the difference between rainfall and drainage (or drainage and run-off) can be equated to the evaporation of the period. As drainage continued for several days after rain it was not always possible to decide which was the last rainfall causing drainage, and there are inevitable uncertainties in the estimation of $(R - D)$ per day as a result. As elsewhere, all estimates of evaporation are very much dependent upon the drain gauge receiving the same amount of rain as the rain gauge.

The values of $R - D$ for gauges I and II (6 ft. and 3 ft. bare) usually agreed closely and there was general consistency in the performance of gauges II and IV. A condensed summary for 2 years shows the order of evaporation per day from all four; further analysis will be restricted to the records for gauge I.

TABLE 11. COMPARATIVE EVAPORATION AT PUSA

period	R/day (in.)	$(R - D)/\text{day}$ (in.)			
		I (6'B)	II (6'C)	III (3'B)	IV (3'C)
1911					
8-18 July	0.34	0.17	0.24	0.15	0.23
19 July-25 Aug.	0.47	0.16	0.37	0.15	0.35
26 Aug.-26 Sept.	0.27	0.12	0.24	0.12	> 0.27
27 Sept.-13 Oct.	0.22	0.12	0.11	0.10	no D
1922					
2-26 July	0.72	0.11	0.22	0.08	0.13
27 July-9 Aug.	0.53	0.09	0.21	0.05	?
10-20 Aug.	0.24	0.12	0.20	0.10	?
21 Aug.-23 Sept.	0.21	0.09	0.22	0.06	0.19
29 Sept.-5 Oct.	0.19	0.13	0.19	0.14	> 0.19

Weather observations at Pusa (1911-33) were made at 08.00 hr. and included dry and wet bulb temperatures, air maximum and minimum temperatures, anemometer readings at 08.00 and 08.03 hr., cloud amount, and 'instrumental test observations', the last being the actual readings of the three dry thermometers, presumably expected to be equal when read. These readings never agreed and differences were erratic, ranging up to 3° F, the usual order being dry > max. > min.

Assuming that the anemometer ran continuously between 08.03 hr. one day and 08.00 hr. the next, the run-of-the-wind per day was obtained for all days except when the reading passed through an unknown zero; the height is assumed to be 2 m. and the calibration the same as the Rothamsted instrument (table 2 above). From the mean air temperature and the 08.00 hr. value of dewpoint the value of the mean saturation deficit was obtained. From these, values of E_n were obtained.

The determination of H had to be based on a single cloud estimate per day; comment is unnecessary. There seemed little point in evaluating it for all periods in all years and only two, 1911 and 1922, are considered in detail (table 12). Mean wind speeds (as measured) ranged from 33 to 133 miles/day, mean and 08.00 hr. air temperatures from 81 to 86° F, 08.00 hr. humidity from 87 to 92 % and estimated n/N from 0.00 to 0.64.

(d) *Cropped soil*

Using the annual summary of the Monthly Weather Report, data for 70 stations in the British Isles have been abstracted for the years 1930-39 and long period means obtained for mean air temperature, mean vapour pressure, mean Beaufort wind force and the mean ratios of actual/possible hours of sunshine. From these, values of E_n and H were obtained for each site and values of E_0 derived, using equation (16). Converted to inches per year, an evaporation map of the British Isles was obtained

TABLE 12. ESTIMATED E_B AND MEASURED $(R - D)/\text{DAY}$ FOR
BARE SOIL: PUSA 1911 AND 1922

period	R/day (in.)	E_n/day (in.)	H/day (in.)	E_{16} (in./day)	$0.9E_{16}$ (in.)	$(R - D)/\text{day}$ (in.)
1911						
8-18 July	0.34	0.08	0.11	0.10	0.09	0.17
19 July-29 Aug.	0.46	0.11	0.16	0.15	0.13	0.16
30 Aug.-8 Sept.	0.17	0.17	0.13	0.14	0.13	0.11
9-26 Sept.	0.32	0.08	0.16	0.14	0.12	0.14
27-30 Sept.	0.18	0.07	0.11	0.10	0.09	0.14
1-13 Oct.	0.22	0.09	0.14	0.13	0.11	0.10
1922						
2-20 July	0.80	0.09	0.12	0.11	0.10	0.10
21-26 July	0.45	0.12	0.12	0.12	0.11	0.15
27 July-9 Aug.	0.54	0.12	0.14	0.13	0.12	0.09
10-15 Aug.	0.12	0.04	0.08	0.07	0.06	0.08
16-20 Aug.	0.38	0.12	0.17	0.16	0.14	0.18
21-26 Aug.	0.16	0.07	0.12	0.11	0.10	0.10
27-30 Aug.	0.25	0.09	0.10	0.10	0.09	0.16
31 Aug.-5 Sept.	0.25	0.08	0.12	0.11	0.10	0.13
6-10 Sept.	0.15	0.09	0.22	0.18	0.17	0.13
11-28 Sept.	0.34	0.09	0.14	0.13	0.11	0.14
29 Sept.-5 Oct.	0.19	0.02	0.19	0.14	0.13	0.14

showing the probable value of annual evaporation from open water in exposed sites. From the conclusions in § 8 above one would expect the corresponding value of the annual evaporation from cropped land to be $\frac{4}{3}$ of E_0 if the crops transpired at maximum rates all the year; in practice the rates will be less than this because of the ripening process in annual vegetation and/or the lack of summer rainfall, particularly in south-east England, but in the table below this conversion factor is applied uniformly. The table shows the observed difference between rainfall and runoff for certain catchment areas (Lloyd 1940, 1941, 1942) (these are rather monotonous), the observed difference multiplied by $\frac{4}{3}$, which should be the expected corresponding open water evaporation, and the estimated value of E_0 based on annual mean values of weather elements for stations somewhere near, if not in, the catchment area.

TABLE 13. EVAPORATION FROM CATCHMENT AREAS

catchment	period	mean rainfall-runoff (in./year)	$4/3(R-r)$	estimated E_0 for nearby sites (in./year)
Lea	1928-36	19.2	26	Greenwich, 25 Rothamsted, 20
Thames	1928-36	18.7	25	Kew, 26 Oxford, 24
Severn	1928-36	18.8	25	Ross-on-Wye, 24 Cheltenham, 21 Shrewsbury, 21
Vrnwy	1932-38	19.1	26	Shrewsbury, 21 Sealand, 24 Llandudno, 23
Rivington	1932-38	17.4	23	Stonyhurst, 21 Hutton, 18
Spey	1936	10.3	14	Dalwhinnie, 17

Detailed examination of Rothamsted data has shown that the sum of the twelve monthly estimates exceeds the annual estimate by about 10 %, due to the extra weight which should be given to summer evaporation. A similar increase is to be expected for other sites and should be borne in mind in reading table 13.

10. GENERAL CONCLUSION

A detailed discussion of the data presented in § 9 (b), (c) and (d) would be intolerably long, and much of it would be concerned with the adequacy of the observations rather than the adequacy of the equations on which the estimates are based. The general impression is satisfactory for all three types of surface, and the wide range of climatic regions employed indicates that something of universal significance has been obtained in the results of §§ 3 to 8, although there must inevitably be something of the time and place at which the experimental work was done included in the equations.

Two aspects of evaporation have been under review. There is that of the physicist and mathematician seeking facts to fit a formula; sufficient has emerged to show

possible sources of weakness in the theoretical treatment of both sink strength and energy balance and to show the relative importance of the quantities that must be measured to obtain adequate accuracy in experimental trials. There is also that of the 'practical' man—water engineer or meteorologist—seeking a formula to fit the facts. Formulae have been given and where all the necessary measurements can be made, or values forecast, then reliable evaporation rates can be estimated or predicted. There are still empirical aspects of both sink strength and energy balance estimates and until these are removed there must always be some doubt about the possibility of successful translation in space or time of the formulae.

The work described in the preceding pages is an extension of research carried out at Rothamsted Experimental Station before 1941. It was resumed in 1944 at the request of the Meteorological Office, and it is a pleasure to be able to record my appreciation of the assistance given by several branches of the Office in the form of equipment, information and advice. I am particularly indebted for many helpful discussions to Mr C. S. Durst of the Meteorological Office, and to my colleague, Dr R. K. Schofield. To the Director of the Meteorological Office and the Meteorological Research Committee I am grateful for the helpful reception given to the report on which this paper is based and for permission to publish it.

Finally, this work could not have been done at short notice if the basic equipment of the enclosure had not been available: to Dr B. A. Keen, F.R.S., until recently Head of the Physics Department at Rothamsted, especially grateful acknowledgment is due for the foresight that provided the installation with full knowledge that it would be many years before the soil would be fit for experimental work.

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Relaxation methods applied to engineering problems

XIII. The flexure and extension of perforated elastic plates

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The theory given in Part VIIA (1941) for a flat plate having a single external boundary is here extended to allow for internal boundaries (holes) at which, as well as at the external boundary, either tractions or displacements may be specified. Such holes entail appreciable complication, more especially when boundary tractions are specified and do not form an equilibrating system at each hole severally: 'orthodox' studies (e.g. by Bickley, Green, Howland, Jeffery) have been restricted to simple shapes (e.g. one or more circular holes in a plate having infinite extension). But any shape can be treated by Relaxation Methods, without excessive labour and with all the accuracy that has practical value. A worked example (stresses in a loaded tie-bar) shows that holes may entail a cyclic form for Airy's stress-function χ .

INTRODUCTION AND SUMMARY

1. Part VIIA of this series (Fox & Southwell 1941) dealt both with flexure and extension of flat elastic plates. Starting from a résumé of accepted theory, it showed both kinds of straining to present the same computational problem, of which it distinguished two main cases:

Case 'A' calls for solution of a biharmonic equation typified by

$$D\nabla^4 w = Z(x, y) \quad (1)$$

(Z being specified), together with boundary conditions (imposed on w) which specify displacements in the flexural, tractions in the extensional problem.

Case 'B' calls for solution of two simultaneous equations, typified by

$$\left. \begin{aligned} \frac{\partial \Delta}{\partial x} + A(\nabla^2 u + \rho X/\mu) &= 0 \\ \frac{\partial \Delta}{\partial y} + A(\nabla^2 v + \rho Y/\mu) &= 0 \end{aligned} \right\} \cdot \left(\Delta \equiv \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right), \quad (2)$$

in which all quantities except u and v are specified, together with boundary conditions (imposed on u and v) which specify displacements in the extensional, tractions in the flexural problem.

For these two cases Part VIIA proposed two different methods, both involving the relaxational technique. Either could deal with 'mixed' boundary conditions (specifying displacements at some points, tractions at others), and the question, which of the two is preferable, was left to the test of experience.

2. Another matter not discussed in Part VIIA is treated in the present paper: namely, the case presented when a plate is perforated so as to have internal boundaries (holes) at which—as well as at its external boundary—either tractions or

displacements are specified. Here too the flexural and the extensional problem are analogous so that (when 'mixed' boundary conditions are excluded) two cases 'A' and 'B' (§1) arise. Case 'B' is not exemplified, being of rare occurrence in practice and because it presents no computational problem that is not confronted in Case 'A'. Case 'A' has practical importance, and in this paper is discussed in fuller detail: an extensional example (stresses in a loaded tie-bar) shows that holes may entail a cyclic form for Airy's stress-function χ .

The whole investigation would have had only academic interest if Relaxation Methods did not provide an alternative to orthodox biharmonic analysis, for in that analysis holes entail such complication that only the simplest shapes are tractable. By contrast, for Relaxation Methods all shapes are tractable with equal accuracy and with roughly equal labour (depending on the number of the holes). In bringing perforated plates within their range, this paper removes their one outstanding disadvantage as compared with the photo-elastic technique.

I. HOLES IN RELATION TO CASE 'A' OF THE FLEXURAL PROBLEM

3. In Case 'A' of the flexural problem the aim is to determine the transverse deflexions (w) of the middle surface, and from these the stresses. The governing equation is

$$D\nabla^4 w = Z(x, y) \quad (1) \text{ bis}$$

(D denoting the flexural rigidity), and the boundary conditions (usually) specify values of w , $\partial w/\partial x$ and $\partial w/\partial y$. They may do this either 'absolutely' (so that at the outset all boundary values of w , $\partial w/\partial x$, $\partial w/\partial y$ are known) or 'relatively' in the sense that at each internal boundary something in the nature of a clamp may operate to impose local variations of deflexion and of slope, the clamp itself being free to move under the action of known external actions. When the specification is 'absolute', internal boundaries present no special problem. When it is 'relative', a displacement of its 'clamp' defined by

$$w_{cl} = A + Bx + Cy \quad (3)$$

may require corresponding additions to w , $\partial w/\partial x$ and $\partial w/\partial y$ at an internal boundary, and we have the problem of determining the constants A , B , C .

4. Equation (1) being linear, solutions can be superposed. Accordingly we first examine the action of the clamp held fixed by imposing the relative displacements and (when we have solved the problem thus presented) deducing the consequent actions on the clamp from the boundary tractions. These tractions are given by

$$\left. \begin{aligned} G &= -D \left[\nabla^2 w - (1 - \sigma) \left(\frac{\partial^2 w}{\partial s^2} + \frac{1}{\rho} \frac{\partial w}{\partial \nu} \right) \right], \\ N - \frac{\partial H}{\partial s} &= -D \left[\frac{\partial}{\partial \nu} \nabla^2 w + (1 - \sigma) \left(\frac{\partial}{\partial s} \left(\frac{\partial^2 w}{\partial s \partial \nu} - \frac{1}{\rho} \frac{\partial w}{\partial s} \right) \right) \right], \end{aligned} \right\} \quad (4)$$

which are (6) of Part VIIA. G , H and N denote, respectively, the line-intensities of flexural moment, torsional moment and transverse (shearing) force, the senses being as shown in figure 1. The fact, that N and H cannot be specified separately was first explained by Kirchhoff (cf., e.g., Love 1927, p. 27).

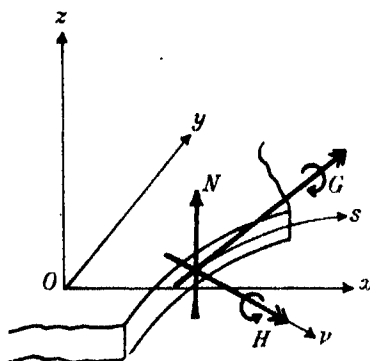


FIGURE 1

The action of the clamp upon the plate will comprise a transverse force Z in the direction of z , and moments L and M about axes parallel to x and y , given by

$$\begin{aligned} Z &= \oint N ds, \quad L = \oint \{H \cos(x, \nu) - G \sin(x, \nu) + yN\} ds, \\ M &= \oint \{G \cos(x, \nu) + H \sin(x, \nu) - xN\} ds, \end{aligned} \quad (5)$$

in which the integrations are to be taken round the whole of the internal boundary. With G , H , N given their expressions (4), and when account is taken of the fact that w and its differentials are single-valued, the expressions (5) can be identified with*

$$\begin{aligned} Z &= -D \oint \frac{\partial}{\partial \nu} \nabla^2 w ds, \quad L = -D \oint \left[y \frac{\partial}{\partial \nu} - \sin(x, \nu) \right] \nabla^2 w ds, \\ M &= +D \oint \left[x \frac{\partial}{\partial \nu} - \cos(x, \nu) \right] \nabla^2 w ds. \end{aligned} \quad (6)$$

The orthodox approach

5. For equilibrium of the clamp, external forces must operate to supply these actions which it transmits to the plate; so to the 'relative' displacements must be added displacements, due to movement of the clamp, such that Z , L , M as given by (6) are the resultants of the known external actions (§ 3). In an orthodox treatment

* It is to be remembered that $\frac{1}{\rho} = \frac{d}{ds}(x, \nu)$.

w would be found by a synthesis of (for one internal boundary) four partial solutions: that is, by writing

$$w = w_0 + Aw_A + Bw_B + Cw_C \quad (7)$$

(where A, B, C are the constants so denoted in §3) and using (6) to deduce corresponding expressions for Z, L, M of the type

$$Z = Z_0 + AZ_A + BZ_B + CZ_C. \quad (8)$$

These last give three equations by means of which A, B, C can be evaluated, and then all terms in (7) are known. In that expression w_0 is the solution obtained when $A = B = C = 0$ in (3), so that the clamp is fixed; w_A is obtained by making $Z = 0$ in (1) and $A = 1, B = C = 0$ in (3); and so on.

When there is more than one internal boundary, each clamp independently can undergo a rigid-body displacement, so N clamps entail $3N$ constants of the type A, B, C , all of which enter into $3N$ expressions of the type of (8). On this account the labour entailed is great when the plate has many holes.

The relaxational approach

6. By contrast, Relaxation Methods dispense with this synthesis and obtain the wanted solution by a single computation. This is because the actions on a clamp can be 'liquidated' by 'block displacements' used in the usual way. Having the standard 'relaxation pattern', it is easy to deduce the changes made in Z, L, M by unit displacement or rotations of the clamp as a whole: these are the 'block displacements' whereby Z, L and M are 'liquidated' at the cost of new 'residuals' at nodal points within the plate. Analogous treatment was employed in Part III (Christopherson & Southwell 1938) to solve the torsion problem of St Venant for a multiply-connected section.

II. HOLES IN RELATION TO CASE 'A' OF THE EXTENSIONAL PROBLEM

7. In Case 'A' of the extensional problem, boundary *tractions* are specified, and the treatment recommended in Part VIIA entails a use of Airy's stress-function χ . In all cases which have practical importance the body-forces can be derived from a potential Ω . Then, the governing equation is†

$$\nabla^2\{\nabla^2\chi + (1-\sigma)\rho\Omega\} = 0, \quad (9)$$

ρ denoting the (uniform) density of the plate; the stress components have the expressions

$$X_x = \frac{\partial^2\chi}{\partial y^2} + \rho\Omega, \quad X_y = -\frac{\partial^2\chi}{\partial x\partial y}, \quad Y_y = \frac{\partial^2\chi}{\partial x^2} + \rho\Omega, \quad (10)$$

† Conditions of *plane stress* are here assumed. The treatment of plane strain is similar, but the factor $(1-\sigma)$, in (9), must be replaced by $(1-2\sigma)/(1-\sigma)$ (cf. Part VIIA, §5).

and the boundary conditions can be stated as imposing specified values on X_v , Y_v , where

$$X_v - \rho\Omega \cos(x, v) = \frac{\partial}{\partial s} \left(\frac{\partial \chi}{\partial y} \right), \quad Y_v - \rho\Omega \sin(x, v) = -\frac{\partial}{\partial s} \left(\frac{\partial \chi}{\partial x} \right) \quad (11)$$

(the senses being as shown in figure 2). The mathematical problem is to determine χ as defined by (9) and (11).

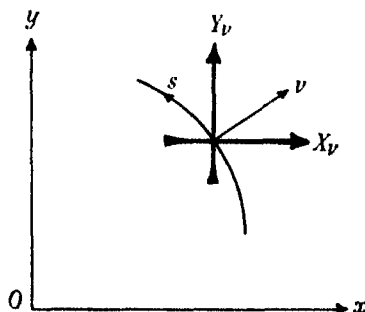


FIGURE 2

Circumstances entailing cyclic constants

8. An immediate consequence of perforations is that χ , $\frac{\partial \chi}{\partial x}$, $\frac{\partial \chi}{\partial y}$ need not be single-valued as (on the tacit assumption of a single boundary) they were shown to be in Part VIIA, § 7. According to (11), on any closed boundary

$$\frac{\partial \chi}{\partial y} = \int \{X_v - \rho\Omega \cos(x, v)\} ds, \quad (i)$$

so $\partial \chi / \partial y$ is cyclic unless

$$\oint \{X_v - \rho\Omega \cos(x, v)\} ds = 0, \quad (12)$$

—i.e. (by Green's transformation) unless

$$= \oint X_v ds - \iint \rho \frac{\partial \Omega}{\partial x} dx dy = \oint X_v ds + \iint \rho X dx dy = 0 \quad (ii)$$

when the surface integral is taken over the whole area of the plate. Equation (12) is satisfied when there is no internal boundary, for then the quantity on the right of (ii) must vanish for equilibrium. If on the other hand the plate is perforated, equilibrium requires (12) to be satisfied only when the contour integral relates to its whole perimeter: it need not hold in respect of any one internal boundary.

Similarly, according to (11), on any closed boundary

$$-\frac{\partial \chi}{\partial x} = \int \{Y_v - \rho\Omega \sin(x, v)\} ds, \quad (iii)$$

so is cyclic unless

$$\oint \{Y_v - \rho\Omega \sin(x, v)\} ds = 0. \quad (13)$$

Equation (13) must be satisfied, for equilibrium, in respect of the boundary of a singly-connected region; but it need not hold in respect of any one internal boundary.

Finally,
$$\frac{\partial \chi}{\partial s} = \frac{\partial y}{\partial s} \frac{\partial \chi}{\partial y} + \frac{\partial x}{\partial s} \frac{\partial \chi}{\partial x},$$

so
$$\begin{aligned} \chi &= y \frac{\partial \chi}{\partial y} + x \frac{\partial \chi}{\partial x} - \int \left(y \frac{\partial^2 \chi}{\partial s \partial y} + x \frac{\partial^2 \chi}{\partial s \partial x} \right) ds, \\ &= y \frac{\partial \chi}{\partial y} + x \frac{\partial \chi}{\partial x} + \int [xY_v - yX_v - \{x \sin(x, v) - y \cos(x, v)\} \rho \Omega] ds \end{aligned} \quad (14)$$

according to (11). When there is only an external boundary, Green's transformation can be used to show that

$$\begin{aligned} \oint [xY_v - yX_v - \{x \sin(x, v) - y \cos(x, v)\} \rho \Omega] ds \\ = \oint (xY_v - yX_v) ds + \iint (xY - yX) dx dy = 0 \end{aligned} \quad (15)$$

for equilibrium; so then this expression for χ is single-valued. But (15) need not hold in respect of any one internal boundary; so there χ as well as $\partial \chi / \partial x$ and $\partial \chi / \partial y$ may be cyclic.

9. To summarize, $\partial \chi / \partial x$ is cyclic unless (13), $\partial \chi / \partial y$ unless (12), and χ unless (15) is satisfied for each internal boundary severally. On any boundary for which (12) is satisfied, the total action has no resultant in the direction of x ; on any for which (13) is satisfied, it has no resultant in the direction of y ; and on any for which (15) is satisfied, it has no resultant moment about Oz . Thus the relaxation process (since it requires the boundary values of $\partial \chi / \partial x$, $\partial \chi / \partial y$ and χ to be specified uniquely) will not be feasible unless the tractions at each internal boundary, severally, are self-equilibrating. If this condition is not satisfied in the problem as presented, the problem must be modified by removal of the cyclic part of χ .

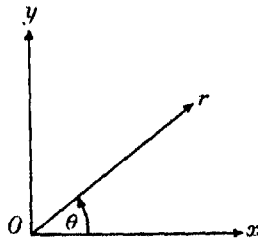


FIGURE 3

Procedure for elimination of cyclic constants

10. Consider in this connexion, and for the notation which is indicated in figure 3, the functions

$$\chi_x = -\frac{r}{2\pi} \theta \sin \theta, \quad \chi_y = \frac{r}{2\pi} \theta \cos \theta, \quad \chi_N = -\frac{\theta}{2\pi}, \quad (16)$$

all of which satisfy (9) with $\Omega = 0$ —i.e. when no body-force is operative. The corresponding stresses are single-valued and have no singularity except at the origin of

co-ordinates, therefore make no contribution to (12), (13) or (15) in respect of any contour which does not enclose that point; but for each function one or more of χ , $\partial\chi/\partial x$, $\partial\chi/\partial y$ is cyclic, as shown in table 1. In that table X , Y , N denote the total forces and couples entailed by the functions—i.e. the contributions which they make to the left-hand sides of (12), (13) and (15), respectively, for any closed circular boundary surrounding the origin of co-ordinates.

TABLE 1

	(i)	(ii)	(iii)
	χ_x	χ_r	χ_θ
$\widehat{rr} = \frac{1}{r} \frac{\partial\chi}{\partial r} + \frac{1}{r^2} \frac{\partial^2\chi}{\partial\theta^2}$	$-\frac{\cos\theta}{\pi r}$	$-\frac{\sin\theta}{\pi r}$	0
$\widehat{\theta\theta} = \frac{\partial^2\chi}{\partial r^2}$	0	0	0
$\widehat{r\theta} = -\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial\chi}{\partial\theta} \right)$	0	0	$-\frac{1}{2\pi r^2}$
$X = -\int_0^{2\pi} r(\widehat{rr} \cos\theta - \widehat{r\theta} \sin\theta) d\theta$	1	0	0
$Y = -\int_0^{2\pi} r(\widehat{r\theta} \sin\theta + \widehat{\theta\theta} \cos\theta) d\theta$	0	1	0
$N = -\int_0^{2\pi} r^2 \cdot \widehat{r\theta} \cdot d\theta$	0	0	1
$\frac{\partial\chi}{\partial x} = \cos\theta \frac{\partial\chi}{\partial r} - \frac{\sin\theta}{r} \frac{\partial\chi}{\partial\theta}$	$\frac{\sin^2\theta}{2\pi}$	$\left(\frac{\theta - \frac{1}{2} \sin 2\theta}{2\pi} \right)^*$	$\frac{\sin\theta}{2\pi r}$
$\frac{\partial\chi}{\partial y} = \sin\theta \frac{\partial\chi}{\partial r} + \frac{\cos\theta}{r} \frac{\partial\chi}{\partial\theta}$	$-\left(\frac{\theta + \frac{1}{2} \sin 2\theta}{2\pi} \right)^*$	$\frac{\cos^2\theta}{2\pi}$	$-\frac{\cos\theta}{2\pi r}$
χ	$-\frac{r\theta \sin\theta}{2\pi}$	$\frac{r\theta \cos\theta}{2\pi}$	$-\left(\frac{\theta}{2\pi} \right)^*$

* Cyclic quantities.

The corresponding actions on other internal boundaries will not be affected because those boundaries do not enclose the origin: consequently it is easy to attach such multipliers to the expressions (16) as will make those 'singularity solutions' account for the unbalanced resultants of the tractions on each internal boundary severally. (They will also entail tractions on other boundaries, but these will be self-equilibrating.) Thus a problem as presented can be modified so that at every boundary $\partial\chi/\partial x$, $\partial\chi/\partial y$ and χ are single-valued; and apart from constants of integration all three quantities will be known.

Significance of the constants of integration in the boundary values of $\partial\chi/\partial x$, $\partial\chi/\partial y$ and χ

11. The constants do not matter when (as in Part VIIA) the plate considered has no perforations; for then they merely entail an addition to χ which, being linear in x and y , has no effect upon the stresses. But they matter in relation to holes, exactly

as in the flexural problem (§3) those constants mattered which defined the rigid-body displacement of the clamp (though now for a physically different reason). Thus a problem still remains.

Conditions of plane stress are contemplated in the argument which follows, but with an altered value for σ it will hold in circumstances of plane strain.* The reason why the constants of integration matter now is that, while any values will define a solution in which χ (and hence all stresses and strains) are single-valued, *this solution may entail self-straining*, which is always a possibility in multiply-connected bodies (cf., e.g., Southwell 1941, Chap. III). Consequently the relations which fix the values of the constants are to be sought in the conditions for compatibility of strain.

12. Expressed in terms of displacement the strain-components (necessarily single-valued) are

$$e_{xx} = \frac{\partial u}{\partial x}, \quad e_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}, \quad e_{yy} = \frac{\partial v}{\partial y}, \quad (i)$$

and the rotation ϖ is given by

$$2\varpi = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}. \quad (ii)$$

On physical grounds u , v and ϖ must be single-valued, and according to (i) and (ii)

$$\frac{\partial v}{\partial x} = \varpi + \frac{1}{2}e_{xy}, \quad \frac{\partial u}{\partial y} = \frac{1}{2}e_{xy} - \varpi. \quad (iii)$$

Therefore the relations

$$\frac{\partial}{\partial y}(\varpi + \frac{1}{2}e_{xy}) = \frac{\partial^2 v}{\partial y \partial x} = \frac{\partial}{\partial x}e_{xy}, \quad \frac{\partial}{\partial x}(\frac{1}{2}e_{xy} - \varpi) = \frac{\partial^2 u}{\partial x \partial y} = \frac{\partial}{\partial y}e_{xy}, \quad (iv)$$

must be satisfied throughout any region in which u and v are single-valued; and hence the relation

$$\frac{\partial^2}{\partial x^2}e_{xy} - \frac{1}{2}\frac{\partial^2}{\partial x \partial y}e_{xy} = \frac{\partial^2 \varpi}{\partial x \partial y} = \frac{1}{2}\frac{\partial^2}{\partial y \partial x}e_{xy} - \frac{\partial^2}{\partial y^2}e_{xy} \quad (v)$$

must be satisfied throughout any region in which ϖ is single-valued.

Expressed in terms of χ the relation (v) is equivalent to (9) of §7, so it will be satisfied by any solution of that equation. In relation to a multiply-connected region, however, though necessary it is not sufficient, since it merely requires ϖ , if cyclic, to have the same cyclic constant at every point. To make the constant zero the condition

$$\oint \frac{d\varpi}{ds} ds = \oint \left\{ \cos(x, \nu) \frac{\partial \varpi}{\partial y} - \sin(x, \nu) \frac{\partial \varpi}{\partial x} \right\} ds = 0$$

must hold for each internal boundary severally; that is, by (iv), the condition

$$\oint \left\{ \cos(x, \nu) \left(\frac{\partial}{\partial x}e_{xy} - \frac{1}{2}\frac{\partial}{\partial y}e_{xy} \right) + \sin(x, \nu) \left(\frac{\partial}{\partial y}e_{xy} - \frac{1}{2}\frac{\partial}{\partial x}e_{xy} \right) \right\} ds = 0,$$

* Cf. footnote to §7.

which, expressed in terms of stresses and thence of χ , is

$$\oint \frac{\partial}{\partial \nu} \{ \nabla^2 \chi + (1 - \sigma) \rho \Omega \} ds = 0. \quad (17)$$

When (17) holds in respect of every internal boundary, the fact that (9), § 7, is satisfied implies that it will also hold at the external boundary.

13. Similar considerations apply in respect of u and v : having satisfied (17) we have a non-cyclic solution for ϖ which makes the relations (iv) compatible throughout the perforated plate; and when (iv) are satisfied then u and v , if cyclic, must have the same cyclic constant throughout. The conditions that u and v shall be non-cyclic are, respectively,

$$\oint \frac{du}{ds} ds = 0 \quad \text{and} \quad \oint \frac{dv}{ds} ds = 0 \quad (\text{vi})$$

for each internal boundary severally. They may be transformed on the understanding that (i)–(iv) are satisfied and ϖ is single-valued.

$$\begin{aligned} \text{Thus} \quad \oint \frac{du}{ds} ds &= \oint \left(l \frac{\partial u}{\partial y} - m \frac{\partial u}{\partial x} \right) ds \\ &= \oint \{ l(\tfrac{1}{2} e_{xy} - \varpi) - m e_{xx} \} ds \end{aligned}$$

according to (iii); therefore, since $l = \partial y / \partial s$ and ϖ is single-valued, a condition equivalent to the first of (vi) is

$$\begin{aligned} 0 &= \oint \left\{ l \left(\tfrac{1}{2} e_{xy} + y \frac{\partial \varpi}{\partial y} \right) - m \left(e_{xx} + y \frac{\partial \varpi}{\partial x} \right) \right\} ds, \\ &= \oint \left\{ l \left[\tfrac{1}{2} e_{xy} + y \left(\frac{\partial}{\partial x} e_{xy} - \frac{1}{2} \frac{\partial}{\partial y} e_{xy} \right) \right] - m \left[e_{xx} + y \left(\frac{1}{2} \frac{\partial}{\partial x} e_{xy} - \frac{\partial}{\partial y} e_{xx} \right) \right] \right\} ds \end{aligned}$$

according to (iv). Expressed in terms of stresses and thence of χ , this equation becomes

$$\oint \left\{ \left[y \frac{\partial}{\partial \nu} + \frac{\partial x}{\partial s} \right] \{ \nabla^2 \chi + (1 - \sigma) \rho \Omega \} - (1 + \sigma) \frac{\partial}{\partial s} \left(\frac{\partial \chi}{\partial x} \right) \right\} ds = 0,$$

or (since x and $\partial \chi / \partial x$ are single-valued)

$$\oint \left[y \frac{\partial}{\partial \nu} - x \frac{\partial}{\partial s} \right] \{ \nabla^2 \chi + (1 - \sigma) \rho \Omega \} ds = 0. \quad (\text{vii})$$

Clearly, equation (vii) is equivalent to

$$\oint \left[y \frac{\partial}{\partial \nu} - \sin(x, \nu) \right] \{ \nabla^2 \chi + (1 - \sigma) \rho \Omega \} ds = 0, \quad (18)$$

which accordingly is equivalent to the first of (vi); and similar treatment shows the second of (vi) to be equivalent to

$$\oint \left[x \frac{\partial}{\partial \nu} - \cos(x, \nu) \right] \{ \nabla^2 \chi + (1 - \sigma) \rho \Omega \} ds = 0. \quad (19)$$

If satisfied in respect of every internal boundary, (18) and (19) will also be satisfied in respect of the external boundary. For the sum for all boundaries of the contour integral in (18) has, by Green's theorem, the value

$$\iint y \nabla^2 \{ \nabla^2 \chi + (1 - \sigma) \rho \Omega \} dx dy = 0,$$

since (9) is satisfied; and a similar argument holds in respect of (19).

Orthodox and relaxational treatment

14. Orthodox treatment, though it does not require that cyclic constants be eliminated, normally presents insuperable difficulty. For Relaxation Methods the elimination is necessary: then, however, comparison of (17)–(19) with (6), § 4, shows that the modified problem can be solved by taking advantage of the analogy which relates χ in the extensional with w in the flexural problem. *Thinking now of χ as representing flexural displacement*, we may envisage ‘clamps’ which specify χ , $\partial\chi/\partial x$ and $\partial\chi/\partial y$ ‘relatively’ in the sense of § 3, but which can also undergo rigid-body displacements and thereby impose constants of integration. Now, according to (17)–(19), the clamps must ‘float’ because the forces acting on each severally are in equilibrium. In other respects the relaxational procedure is unaltered.

III. HOLES IN RELATION TO CASE ‘B’ OF THE EXTENSIONAL PROBLEM

15. In Case ‘B’ of the extensional problem the aim is to determine component displacements u and v which are governed by (2), § 1, and of which the boundary values are specified. As in § 3 the specification may be either ‘absolute’ (so that at the outset u and v have known values at every boundary point) or ‘relative’ in the sense that a ‘clamp’ which imposes known displacements at an internal boundary is itself free to move as a rigid body (now, in the plane of the plate) under the action of external forces. When the specification is ‘absolute’, internal boundaries present no special problem. When it is ‘relative’, three constants are required to define the (small) rigid-body displacement of any clamp, since the most general form of this displacement is given by

$$u_{cl} = A - Cy, \quad v_{cl} = B + Cx; \quad (20)$$

so here, as in § 3, the solution must determine three constants (A , B , C) from the known external forces on each clamp.

The relevant formulae are

$$X = \oint X_r ds, \quad Y = \oint Y_r ds, \quad N = \oint (xY_r - yX_r) ds, \quad (21)$$

in which X, Y, N are the (specified) external forces on any particular clamp, and the contour integrals extend to its whole perimeter (i.e. to the internal boundary in question); with

$$\left. \begin{aligned} X_v &= lX_x + mX_y, & Y_v &= lX_y + mY_x, \\ \text{in which } l &\equiv \cos(x, \nu) = \frac{\partial y}{\partial s}, & m &\equiv \sin(x, \nu) = -\frac{\partial x}{\partial s}, \end{aligned} \right\} \quad (22)$$

and

$$AX_x/\mu = \Delta + A\left(\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y}\right), \quad X_v/\mu = \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right), \quad AY_v/\mu = \Delta + A\left(\frac{\partial v}{\partial y} - \frac{\partial u}{\partial x}\right), \quad (23)$$

in which (as in § 1) μ denotes the modulus of rigidity, Δ stands for $\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right)$, and A is the constant so denoted in equations (2).*

From (21)–(23) it is easy to deduce that

$$\left. \begin{aligned} X/\mu &= \oint \left\{ \frac{\partial u}{\partial \nu} - \frac{\partial v}{\partial s} + l\Delta/A \right\} ds, \\ Y/\mu &= \oint \left\{ \frac{\partial u}{\partial s} + \frac{\partial v}{\partial \nu} + m\Delta/A \right\} ds, \\ N/\mu &= \oint \left\{ x\left(\frac{\partial u}{\partial s} + \frac{\partial v}{\partial \nu}\right) + y\left(\frac{\partial v}{\partial s} - \frac{\partial u}{\partial \nu}\right) + (mx - ly)\Delta/A \right\} ds. \end{aligned} \right\} \quad (24)$$

16. Orthodox treatment (normally very difficult) employs the formulae (24) to deduce the values of A, B, C in (20), and hence of u_{cl}, v_{cl} , in the manner of § 5. A relaxational treatment will use them to deduce the changes made in X, Y, N by unit displacements or rotation of the clamp as a whole, and will proceed to 'liquidate' X, Y, N by 'block displacements', in the manner of § 6. Thus every new problem confronted on account of 'holes' has its parallel in Case 'A' of the flexural problem.

IV. HOLES IN RELATION TO CASE 'B' OF THE FLEXURAL PROBLEM

17. In Case 'B' of the flexural problem the aim is to determine the transverse deflexions (w) of the middle-surface, and from these the stresses, *tractions* being specified by the boundary conditions: that is to say, at every boundary point we have known values of G and of $(N - \partial H/\partial s)$, quantities which are related with w by (4), § 4. In Part VIIA (§§ 9–11) this case was shown to be reducible to a problem mathematically identical with Case 'B' of the extensional problem (§ 15), and like that problem to be tractable (for Relaxation Methods) by a 'two-diagram technique'.

* Cf. footnote to § 7. In terms of Poisson's ratio σ

$$A = 1 - 2\sigma, \text{ under conditions of plane strain,}$$

$$= \frac{1 - \sigma}{1 + \sigma}, \text{ under conditions of plane stress.}$$

First, a quantity $\nabla^2 w_1$ was introduced, defined by

$$\nabla^2(\nabla^2 w_1) = Z/D \quad (14^*) \quad (25)$$

and by the boundary condition $\nabla^2 w_1 = 0$;

then, two quantities U and V of which the boundary values has to be calculated from

$$\begin{aligned} D \frac{\partial U}{\partial s} &= G \sin(x, \nu) - \cos(x, \nu) \left\{ H - \int \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) ds \right\}, \\ -D \frac{\partial V}{\partial s} &= G \cos(x, \nu) + \sin(x, \nu) \left\{ H - \int \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) ds \right\}, \end{aligned} \quad (19^*) \quad (26)$$

and which throughout the plate are governed by the equations

$$\left. \begin{aligned} \frac{\partial \Delta}{\partial x} + A \nabla^2 U + 2X_1 &= 0, \\ \frac{\partial \Delta}{\partial y} + A \nabla^2 V + 2Y_1 &= 0, \end{aligned} \right\} \quad (24^*) \quad (27)$$

in which $A = \frac{1+\sigma}{1-\sigma}$, Δ stands for $\frac{\partial U}{\partial x} + \frac{\partial V}{\partial y}$, (23^*)

and $X_1 = \frac{\partial}{\partial x} \nabla^2 w_1$, $Y_1 = \frac{\partial}{\partial y} \nabla^2 w_1$. (25^*)

These last have the forms of equations (2), § 1, so can be treated as though U and V were extensional displacements and X_1, Y_1 body-forces acting in the plane of the plate, once $\nabla^2 w_1$ has been determined from (25). (This is a standard plane-harmonic problem.) Then, knowing the distributions of U, V and $\nabla^2 w_1$ throughout the plate, we can compute the flexural stresses from

$$\left. \begin{aligned} \frac{\partial^2 w}{\partial y^2} + \sigma \frac{\partial^2 w}{\partial x^2} &= \frac{\partial U}{\partial x} + \nabla^2 w_1, \\ \frac{\partial^2 w}{\partial x^2} + \sigma \frac{\partial^2 w}{\partial y^2} &= \frac{\partial V}{\partial y} + \nabla^2 w_1, \\ -2(1-\sigma) \frac{\partial^2 w}{\partial x \partial y} &= \frac{\partial U}{\partial y} + \frac{\partial V}{\partial x}, \end{aligned} \right\} \quad (26^*) \quad (28)$$

since to obtain the stress-couples it is only necessary to multiply the left-hand sides of (28) by $-D$, $-D$ and $-\frac{1}{2}D$.

Procedure for elimination of cyclic constants (1) from U and V

18. In Part VIIA a plate having only one (external) boundary was contemplated, and it was shown that at this boundary U and V as found from (26) are single-valued, the constants of integration having no importance. Neither conclusion holds (in general) when the plate is perforated. Then, (1) cyclic constants may occur in the expressions for U and V , for reasons similar to those adduced in § 8; (2) constants of integration added to U and V at an internal boundary will entail (at points within

* Asterisks indicate the numbering of equations in Part VIIA.

the plate) changes in the expressions on the right of (28) and consequent changes in the flexural stresses.

19. The cyclic constants can be brought to zero by making appropriate changes in the boundary condition imposed on $\nabla^2 w_1$. Leaving the first of (25) unchanged, we now impose the condition

$$\nabla^2 w_1 = 0$$

at the external boundary only; and at every internal boundary (severally) we require $\nabla^2 w_1$ to be representable by

$$\nabla^2 w_1 = A + Bx + Cy, \quad (29)$$

where A, B, C are constants such that*

$$\left. \begin{aligned} \oint \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) ds &= 0, \\ \oint \left\{ H \cos(x, \nu) - (G + D \nabla^2 w_1) \sin(x, \nu) + y \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) \right\} ds &= 0, \\ \oint \left\{ H \sin(x, \nu) + (G + D \nabla^2 w_1) \cos(x, \nu) - x \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) \right\} ds &= 0. \end{aligned} \right\} \quad (30)$$

Then in equations (26) G has to be replaced by $(G + D \nabla^2 w_1)$;† and remembering that

$$\cos(x, \nu) = \frac{\partial y}{\partial s}, \quad -\sin(x, \nu) = \frac{\partial x}{\partial s}, \quad (22) \text{ bis}$$

we can integrate (26) to obtain the expressions

$$\left. \begin{aligned} DU &= \int \left\{ (G + D \nabla^2 w_1) \sin(x, \nu) - H \cos(x, \nu) - y \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) \right\} ds \\ &\quad + y \int \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) ds, \\ -DV &= \int \left\{ (G + D \nabla^2 w_1) \cos(x, \nu) + H \sin(x, \nu) - x \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) \right\} ds \\ &\quad + x \int \left(N + D \frac{\partial}{\partial \nu} \nabla^2 w_1 \right) ds, \end{aligned} \right\} \quad (31)$$

which make U and V acyclic in virtue of the relations (30).

Those relations may be written in the forms (cf. (6), § 4)

$$\left. \begin{aligned} D \oint \frac{\partial}{\partial \nu} \nabla^2 w_1 ds + Z &= 0, \\ D \oint \left\{ y \frac{\partial}{\partial \nu} \nabla^2 w_1 - \nabla^2 w_1 \sin(x, \nu) \right\} ds + L &= 0, \\ D \oint \left\{ \nabla^2 w_1 \cos(x, \nu) - x \frac{\partial}{\partial \nu} \nabla^2 w_1 \right\} ds + M &= 0, \end{aligned} \right\} \quad (32)$$

* Equations (30) could be obtained by elimination of Z, L, M from (5) and (6), § 4, after w has been replaced by w_1 .

† Cf. the derivation of equations (17*) in Part VIIA.

Z, L, M denoting the resultant force (along Oz) and couples (about axes parallel to Ox and Oy respectively) which the specified tractions **N, G, H** exert upon the boundary in question. When $\nabla^2 w_1$ is given its expression (29), then

$$\left. \begin{aligned} \oint \nabla^2 w_1 \sin(x, \nu) ds &= \oint (A + Bx + Cy) \sin(x, \nu) ds \\ &= -CS, \\ \oint \nabla^2 w_1 \cos(x, \nu) ds &= \oint (A + Bx + Cy) \cos(x, \nu) ds \\ &= -BS, \end{aligned} \right\} \quad (33)$$

by Green's transformation, S denoting the area contained within the internal boundary.*

20. Since $-\nabla^2 w_1$ (within the plate) satisfies the equation

$$D\nabla^2(-\nabla^2 w_1) + Z = 0, \quad (25) \text{ bis}$$

it may be interpreted, in accordance with Prandtl's analogue, as measuring the transverse deflexion of a membrane stretched with uniform tension D and loaded with a transverse pressure Z having the direction of z . On this understanding, $D \frac{\partial}{\partial \nu} \nabla^2 w_1$ measures the line-intensity of the transverse force (in the same direction) which is exerted by the membrane on the boundary, and (32) accordingly require—when combined with (29) and (33)—that a flat plate having the shape of the internal boundary, and given a 'block displacement' such that a point (x, y) moves transversely through a distance $(A + Bx + Cy)$, shall 'float' under the combined effects of the membrane tension and of applied forces and couples measured by **Z, (L + CS)** and **(M + BS)**. Determination of $\nabla^2 w_1$ is thus a plane-potential problem of a type which was discussed in Part III (Christopherson & Southwell 1938). When it has been solved, substitution for $\nabla^2 w_1$ in (31) will render those expressions single-valued. Then, U and V can be computed through the plate from the 'net approximation' to (27), § 17, by the same 'two diagram technique' which yields displacements (u and v) in Case 'B' of the extensional problem (Section III); and the stress-couples, if required, can be deduced from (28).

Procedure for elimination of cyclic constants (2) from w

21. But Part VIIA, in propounding those expressions, did not take note of the possibility that they may not be compatible with the existence of a single-valued displacement (w). This possibility we now consider.

Supposing w to be related with U and V by (28), we can integrate the third of those equations to obtain

$$\left. \begin{aligned} U &= \frac{\partial \psi}{\partial x} - (1 - \sigma) \frac{\partial w}{\partial x}, \\ V &= -\frac{\partial \psi}{\partial y} - (1 - \sigma) \frac{\partial w}{\partial y}, \end{aligned} \right\} \quad (34)$$

* The normal ν is directed into this area.

ψ denoting some unknown function of x and y . Substitution in the first and second equations then gives

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{\partial^2 \psi}{\partial y^2} = \nabla^2 w - \nabla^2 w_1 = \nabla^2 w', \quad (35)$$

showing that ψ is a plane-harmonic function related with the plane-harmonic $\nabla^2 w'$ of Part VIIA.* It also gives

$$\Delta = \frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} = (1 + \sigma) \nabla^2 w' - (1 - \sigma) \nabla^2 w_1. \quad (36)$$

22. According to (34) and (35)

$$\begin{aligned} (1 - \sigma^2) \left[\frac{\partial^2 w}{\partial x^2}, \quad \frac{\partial^2 w}{\partial x \partial y}, \quad \frac{\partial^2 w}{\partial y^2} \right] \\ = (1 + \sigma) \left[\nabla^2 w' - \frac{\partial U}{\partial x}, \quad -\frac{1}{2} \left(\frac{\partial V}{\partial x} + \frac{\partial U}{\partial y} \right), \quad \nabla^2 w' - \frac{\partial V}{\partial y} \right], \\ = \left[\frac{\partial V}{\partial y} - \sigma \frac{\partial U}{\partial x} + (1 - \sigma) \nabla^2 w_1, \quad -\frac{1}{2} (1 + \sigma) \left(\frac{\partial V}{\partial x} + \frac{\partial U}{\partial y} \right), \right. \\ \left. \frac{\partial U}{\partial x} - \sigma \frac{\partial V}{\partial y} + (1 - \sigma) \nabla^2 w_1 \right], \quad (37) \end{aligned}$$

in virtue of (36). Therefore in relation to a closed boundary $\partial w / \partial x$ will be cyclic unless

$$\begin{aligned} 0 &= 2(1 - \sigma^2) \oint \frac{\partial}{\partial s} \left(\frac{\partial w}{\partial x} \right) ds \\ &= - \oint \left\{ (1 + \sigma) \left(\frac{\partial V}{\partial y} + \frac{\partial U}{\partial x} \right) + (1 - \sigma) \sin(x, \nu) (\Delta + 2 \nabla^2 w_1) \right\} ds, \quad (38) \end{aligned}$$

$\partial w / \partial y$ will be cyclic unless

$$\begin{aligned} 0 &= 2(1 - \sigma^2) \oint \frac{\partial}{\partial s} \left(\frac{\partial w}{\partial y} \right) ds \\ &= - \oint \left\{ (1 + \sigma) \left(\frac{\partial V}{\partial x} - \frac{\partial U}{\partial y} \right) - (1 - \sigma) \cos(x, \nu) (\Delta + 2 \nabla^2 w_1) \right\} ds, \quad (39) \end{aligned}$$

and

$$w = \int \frac{\partial w}{\partial s} ds = y \frac{\partial w}{\partial y} + x \frac{\partial w}{\partial x} - \int \left(y \frac{\partial^2 w}{\partial s \partial y} + x \frac{\partial^2 w}{\partial s \partial x} \right) ds$$

* Comparing (34) with (20*), we have

$$\frac{\partial \psi}{\partial x} = \frac{\partial \phi}{\partial y}, \quad -\frac{\partial \psi}{\partial y} = \frac{\partial \phi}{\partial x},$$

showing that (35) is equivalent to

$$\frac{\partial^2 \phi}{\partial x \partial y} = \nabla^2 w', \quad \text{where} \quad \nabla^2 \phi = 0.$$

This is (15*) of Part VIIA.

will (when $\partial w/\partial x$ and $\partial w/\partial y$ are single-valued) be cyclic unless

$$\begin{aligned}
 0 &= 2(1-\sigma^2) \oint \left\{ \cos(x, \nu) \left(y \frac{\partial^2 w}{\partial y^2} + x \frac{\partial^2 w}{\partial y \partial x} \right) - \sin(x, \nu) \left(y \frac{\partial^2 w}{\partial x \partial y} + x \frac{\partial^2 w}{\partial x^2} \right) \right\} ds, \\
 &= \oint \left[(1-\sigma) \{ y \cos(x, \nu) - x \sin(x, \nu) \} (\Delta + 2\nabla^2 w_1) \right. \\
 &\quad \left. + (1+\sigma) \{ y \cos(x, \nu) + x \sin(x, \nu) \} \left(\frac{\partial U}{\partial x} - \frac{\partial V}{\partial y} \right) \right. \\
 &\quad \left. + (1+\sigma) \{ y \sin(x, \nu) - x \cos(x, \nu) \} \left(\frac{\partial U}{\partial y} + \frac{\partial V}{\partial x} \right) \right] ds. \quad (40)
 \end{aligned}$$

23. Writing l, m for $\cos(x, \nu), \sin(x, \nu)$, also A for $(1+\sigma)/(1-\sigma)$ in conformity with (27), we can state the conditions (38)–(40) as

$$\left. \begin{aligned}
 \mathbf{X} \text{ (say)} &\equiv \oint \left\{ \frac{\partial U}{\partial s} + \frac{\partial V}{\partial \nu} + m(\Delta + 2\nabla^2 w_1)/A \right\} ds = 0, \\
 \mathbf{Y} \text{ (say)} &\equiv \oint \left\{ \frac{\partial U}{\partial \nu} - \frac{\partial V}{\partial s} + l(\Delta + 2\nabla^2 w_1)/A \right\} ds = 0, \\
 \mathbf{N} \text{ (say)} &\equiv \oint \left\{ x \left(\frac{\partial U}{\partial s} + \frac{\partial V}{\partial \nu} \right) + y \left(\frac{\partial V}{\partial s} - \frac{\partial U}{\partial \nu} \right) + (mx - ly)(\Delta + 2\nabla^2 w_1)/A \right\} ds = 0.
 \end{aligned} \right\} \quad (41)$$

These, which compare with (24), § 15, show that when U, V are treated as extensional displacements, and when they have been made acyclic (single-valued) by a proper choice of $\nabla^2 w_1$ (§ 19), then to make w and its first derivatives single-valued we must ensure that $\mathbf{X}, \mathbf{Y}, \mathbf{N}$ shall vanish severally for each internal boundary. (Then they will also vanish at the external boundary, since the plate as a whole is in equilibrium. This can be shown by using Green's transformation on (41); for in the resulting surface-integrals the integrands vanish in virtue of (27).)

V. PRINCIPLES OF THE RELAXATIONAL ATTACK

Résumé

24. Excluding cases in which the boundary conditions are 'mixed' (§ 2), we have distinguished four main types of problem concerned with multiply-connected (perforated) plates, and we have seen that in all four the requirements at an internal boundary amount—either in fact or by analogy—to a specification of external actions on a 'clamp' which is free to move.

In Section I (§§ 3–6) such clamps have real existence, and each can execute a rigid-body displacement under external actions $\mathbf{Z}, \mathbf{L}, \mathbf{M}$ of which the expressions in terms of the transverse displacement (w) are given in (6).

In Section II (§§ 7–14) w is replaced by Airy's stress-function χ , which—with its first derivatives $\partial\chi/\partial x$ and $\partial\chi/\partial y$ —need not (like w) be acyclic *because only its second derivatives have physical meaning*. It will be cyclic unless (§ 9) the tractions on each internal boundary, severally, are self-equilibrating; and when it is cyclic, then the

problem as presented must be modified by removal of the cyclic constants—a matter which is discussed in § 10. The modified problem is tractable by Relaxation Methods, once values have been given to the constants of integration which appear in the boundary values of χ , $\partial\chi/\partial x$ and $\partial\chi/\partial y$: the proper values are those which entail no self-straining (§ 11), and these can be determined (§ 14) by the relaxational treatment employed in Section I. That is to say, treating χ as though it represented flexural displacement, and introducing a rigid but mobile ‘clamp’ at each internal boundary, we can interpret the conditions for no self-straining (namely, (17)–(19) of § 13) as requiring every clamp, severally, to ‘float’ in the ideal (flexural) problem.

25. The integral forms of $\mathbf{Z}$, $\mathbf{L}$, $\mathbf{M}$ in (6), and of the boundary conditions (17)–(19), entail no difficulty in their application to a net of finite mesh. In all of them ν stands for the normal directed *outward from the plate*—that is, *into the closed internal boundary*; consequently Green’s transformation applied to (6) yields the expressions

$$\mathbf{Z} = \iint \mathbf{Z}(x, y) dx dy, \quad \mathbf{L} = \iint y \cdot \mathbf{Z}(x, y) dx dy, \quad -\mathbf{M} = \iint x \cdot \mathbf{Z}(x, y) dx dy \quad (42)$$

when (in accordance with (1) of Section I) $\mathbf{Z}(x, y)$ stands for the surface-intensity of a transverse pressure imposed upon the clamp, and when the integrations extend to its whole area; and similar treatment of the surface-integrals in (17)–(19) gives in place of those conditions

$$\mathbf{Z} = \mathbf{L} = \mathbf{M} = 0 \quad (43)$$

when $\mathbf{Z}$, $\mathbf{L}$, $\mathbf{M}$ are given by (42) with

$$\mathbf{Z}(x, y) = \nabla^2 \{ \nabla^2 \chi + (1 - \sigma) \rho \Omega \}. \quad (44)$$

In the flexural problem (Section I), $\mathbf{Z}(x, y)$ is specified at points within the plate, but within the clamp (since this moves as a rigid body) may have any distribution compatible, according to (42), with the specified values of $\mathbf{Z}$, $\mathbf{L}$, $\mathbf{M}$. In the extensional problem (Section II), $\mathbf{Z}(x, y)$ as defined in (44) must vanish at points within the plate, since (44) must be identical with (9), § 7: within the clamp it need not vanish everywhere, but its distribution must give zero values for $\mathbf{Z}$, $\mathbf{L}$, $\mathbf{M}$ according to (42). In either problem, for computation performed on a net of finite mesh, the distributed pressure may be replaced (as is usual) by concentrated forces at nodal points, and the surface integrals in (42) by summations extending to all nodal points within the clamp.

‘Clamps’ also make an appearance in Sections III and IV (in Section IV by analogy); but here they execute rigid-body (‘block’) displacements in the plane of the plate. Our treatment contemplates employment of a ‘two-diagram technique’. The total external action on any clamp is the resultant of $\mathbf{X}$, $\mathbf{Y}$, $\mathbf{N}$ as related with the displacements by (24), § 15.

26. In the extensional problem (Section III), values of X , Y , N are specified. Again ν stands for the normal directed into the internal boundary, so now, applied to (24), Green's transformation gives

$$\left. \begin{aligned} X &= -\frac{\mu}{A} \iint \left(A \nabla^2 u + \frac{\partial \Delta}{\partial x} \right) dx dy = \iint \rho X dx dy, \\ Y &= -\frac{\mu}{A} \iint \left(A \nabla^2 v + \frac{\partial \Delta}{\partial y} \right) dx dy = \iint \rho Y dx dy, \\ N &= -\frac{\mu}{A} \iint \left\{ x \left(A \nabla^2 v + \frac{\partial \Delta}{\partial y} \right) - y \left(A \nabla^2 u + \frac{\partial \Delta}{\partial x} \right) \right\} dx dy = \iint \rho (xY - yX) dx dy, \end{aligned} \right\} \quad (45)$$

ρX , ρY denoting (as in (2), § 1) the components of body-force at points within the clamp, and the integrations (as in § 25) extending to its whole area. Like $Z(x, y)$ in § 25, X and Y may have, within the clamp, any distributions which yield, according to (45), the specified values of X , Y , N ; and may be replaced by concentrated forces at nodal points, in computations performed on nets of finite mesh.

27. Section IV (§§ 17–23) makes Case 'B' of the flexural problem tractable by *analogy* on the lines of §§ 15–16—i.e. by a 'two-diagram technique'; but here additional complication is entailed by the necessity of making the displacement (w) single-valued, and it seems likely that other methods will be found more convenient. The wanted quantities are U and V as governed by (27), § 17, and having boundary values computed from (31), § 19. In the latter, $\nabla^2 w_1$ is an ancillary function introduced in order to make U and V acyclic: within the plate it must satisfy

$$\nabla^2(\nabla^2 w_1) = Z/D, \quad (29) bis$$

and at every internal boundary severally it must be representable by a linear expression

$$\nabla^2 w_1 = A + Bx + Cy,$$

in which A , B , C have values such that (32) are satisfied,—i.e. the relations

$$\left. \begin{aligned} D \oint \frac{\partial}{\partial \nu} \nabla^2 w_1 ds + Z &= 0, \\ D \oint y \frac{\partial}{\partial \nu} \nabla^2 w_1 ds + L + CS &= 0, \\ D \oint x \frac{\partial}{\partial \nu} \nabla^2 w_1 ds - (M + BS) &= 0, \end{aligned} \right\} \quad (46)$$

in which Z , L , M and S have the meanings explained in § 19.

With its sign reversed $\nabla^2 w_1$ can be interpreted as tension in a membrane loaded by transverse pressure Z/D and attached to a light rigid plate at each internal boundary; and since in (46) ν denotes (as in §§ 25 and 26) the normal directed *into*

this rigid plate, Green's transformation applied to the contour integrals gives as equivalent relations

$$\iint \mathbf{Z}(x, y) dx dy = \mathbf{Z}, \quad \iint y \cdot \mathbf{Z}(x, y) dx dy = \mathbf{L}, \quad -\iint x \cdot \mathbf{Z}(x, y) dx dy = \mathbf{M}, \quad (42) \text{ bis}$$

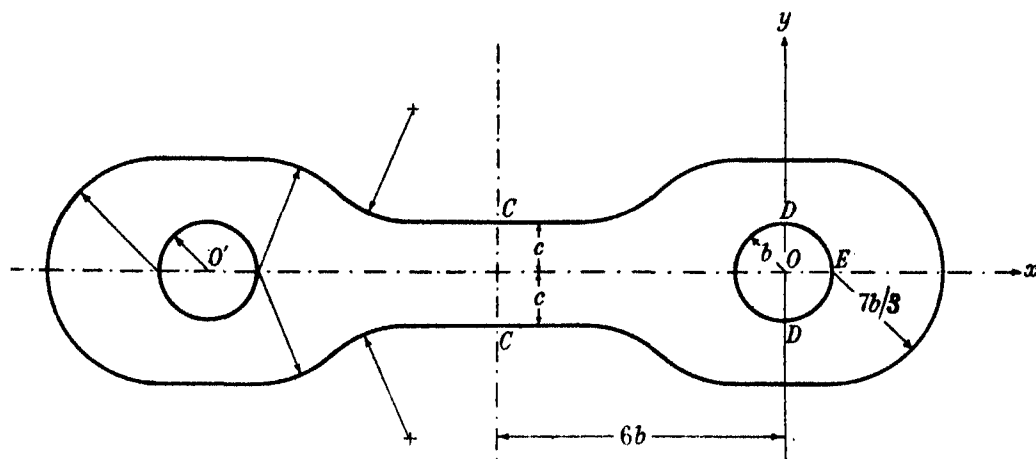
$Z(x, y)$ denoting the pressure within the area of the plate.

28. The principles of the relaxational technique (including a use of 'block displacements' to simulate rigid-body displacements of the 'floating' plates) have been explained in preceding papers of this series, so do not call for discussion here. Details will be explained most easily in relation to a specific example, and we now turn to an extensional problem of the kind discussed in Section II. This will exemplify every process that is entailed by the treatments proposed in Sections I, III and IV, excepting the relatively simple ('plane-harmonic') problem of determining $\nabla^2 w_1$ in Section IV; and the extensional is the most important, practically, of the problems set by perforated plates.

VI. DETAILS OF THE RELAXATIONAL TECHNIQUE

An extensional example

29. The specific problem is shown in figure 4: the stresses induced in a flat plate tension member ('tie') by longitudinal force distributed uniformly over the outer half of either hole. We treat a shape (discussed by Coker & Filon 1931*) in which

**FIGURE 4**

$c = 1.06b$, and assume the centres O, O' (figure 4) to be separated by a distance $12b$. For a tie of this length it may be postulated that the central part is subjected to simple and uniform tension, and its symmetry permits the problem to be stated

* Cf. their figure 6-182, from which the left half of figure 4 is reproduced.

in relation to one-half. Considering the half to right of the centre-line CC in figure 4, we can state the boundary conditions as follows:

$$\left. \begin{array}{ll} \text{along } CC, & X_v = -\frac{1}{2}P/c, \quad Y_v = 0, \\ \text{along the remainder of the outer boundary,} & X_v = Y_v = 0, \\ \text{along the arc } DED \text{ of the circular hole,} & X_v = \frac{1}{\pi} \frac{P}{b}, \quad Y_v = 0, \\ \text{along the remainder of the circular hole,} & X_v = Y_v = 0. \end{array} \right\} \quad (47)$$

P then measures the total tension: the total action on the internal (circular) boundary is a force

$$\mathbf{X} = P, \quad (48)$$

and an equal and opposite force is exerted by the stresses which act across CC . The magnitude of the tension is immaterial, since solutions may be multiplied in accordance with Hooke's law. We give to P and $\mathbf{X}$ (in Table 1) the value 10^3 , in order to eliminate decimals.

We adopt a square-mesh relaxation net of mesh-side $a = \frac{1}{3}b$.

Initial modification of the problem as presented

30. Proceeding in accordance with § 10, we have first to modify the problem as presented so as to leave self-equilibrating tractions on the circular boundary; and for that purpose we employ the first of the functions (16), with origin at O in figure 4, and with the value 10^3 given to P (§ 29).

First, from the wanted solution we have to remove the stresses given in column (i) of Table 1: that is, from the specified boundary tractions (47) we must *deduct*, on the circular hole,

$$X_v (= -\widehat{rr} \cos \theta) = 10^3 \frac{x^2}{\pi r^3}, \quad Y_v (= -\widehat{r\theta} \sin \theta) = 10^3 \frac{xy}{\pi r^3}, \quad (49)$$

and corresponding expressions on the outer boundary; also, throughout the specimen, stress-components given by

$$\begin{aligned} X_x, X_y, Y_y &= \widehat{rr} \times (\cos^2 \theta, \frac{1}{2} \sin 2\theta, \sin^2 \theta) \\ &= -\frac{10^3}{\pi r^4} \times (x^3, x^2y, xy^2). \end{aligned} \quad (50)$$

Figures 5 exhibit values of the deducted stresses at nodal points of the chosen net. The specified boundary tractions are (47) with P replaced by its assumed value 10^3 ; so the modified boundary tractions can be calculated, and from them *acyclic* values of χ , $\partial\chi/\partial x$, $\partial\chi/\partial y$ (that is, of χ at nodal points just inside and just outside the boundaries) to be imposed as a 'relative' specification of the 'clamp' displacements in the flexural analogue of § 14.

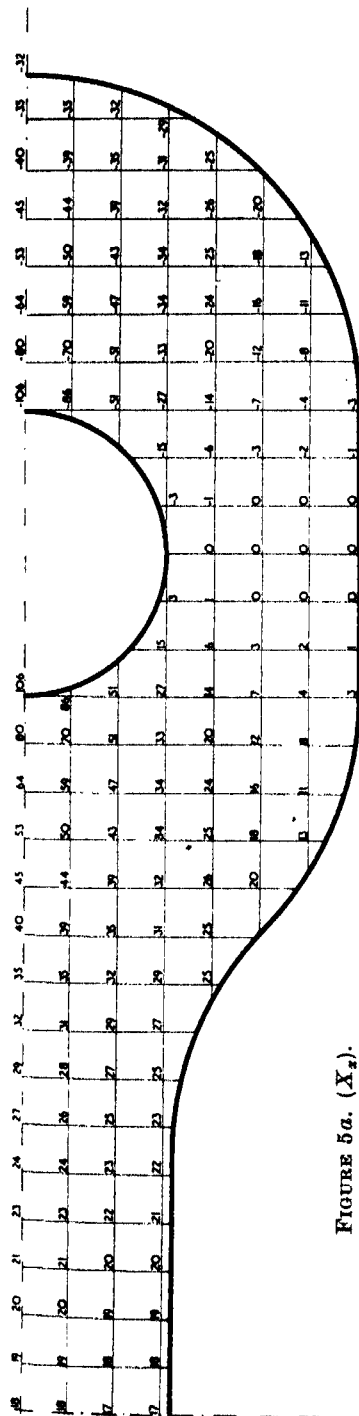


FIGURE 5a. (X_2).

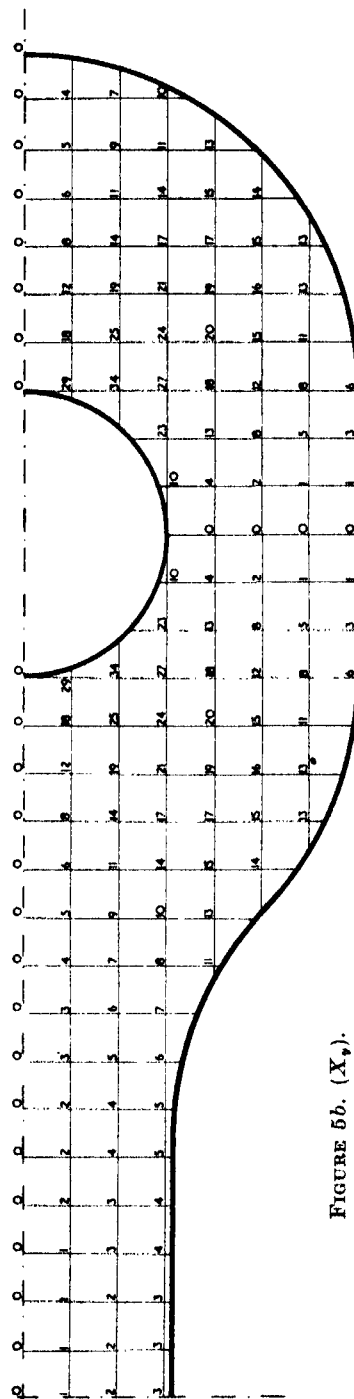


FIGURE 5b. (X_3).

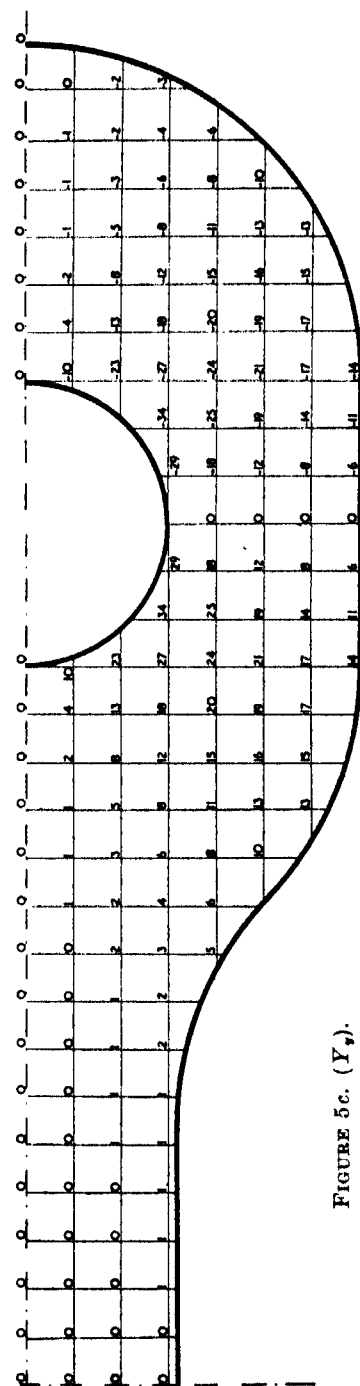


FIGURE 5c. (Y_3).

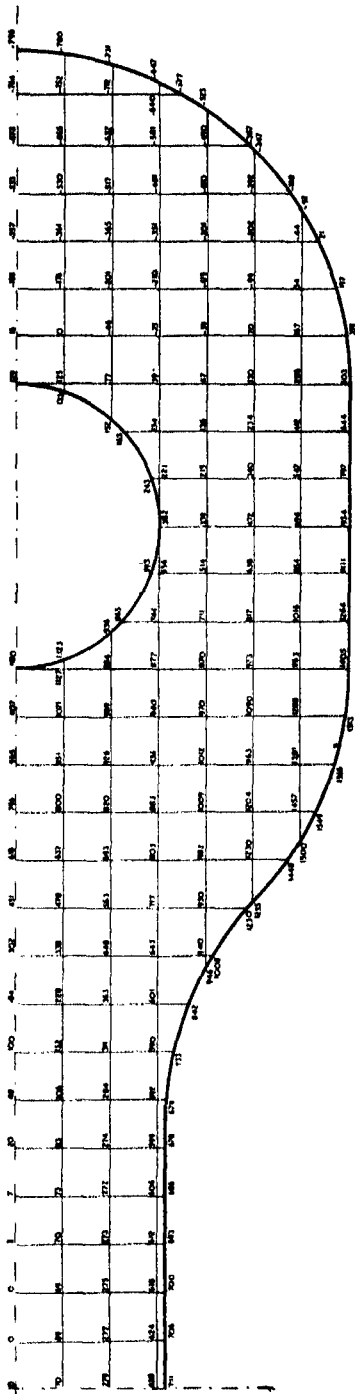


FIGURE 6a. (χ).

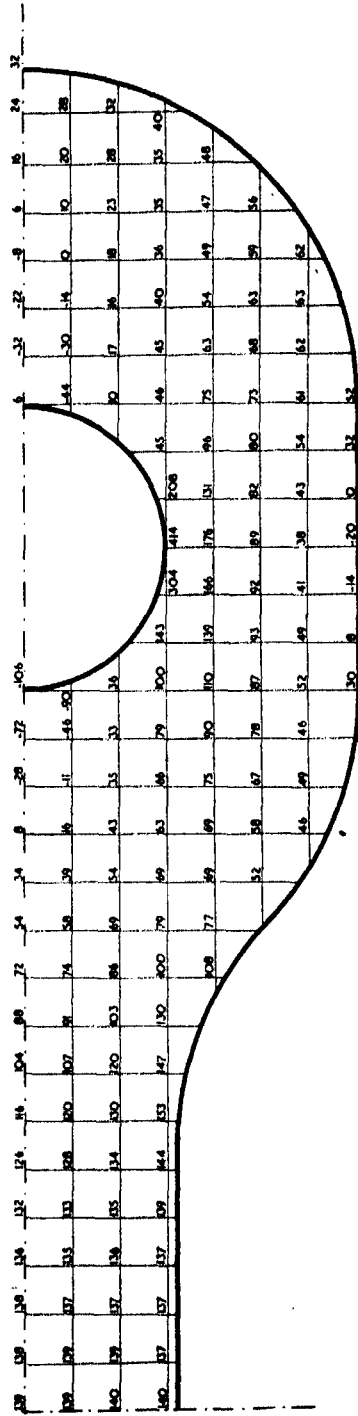


FIGURE 6b. (X_2).

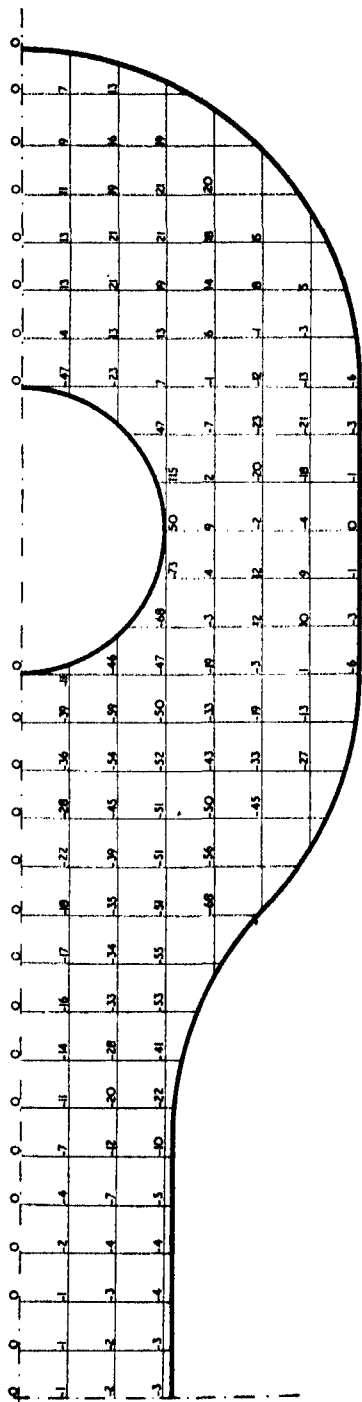


FIGURE 6c. (X).

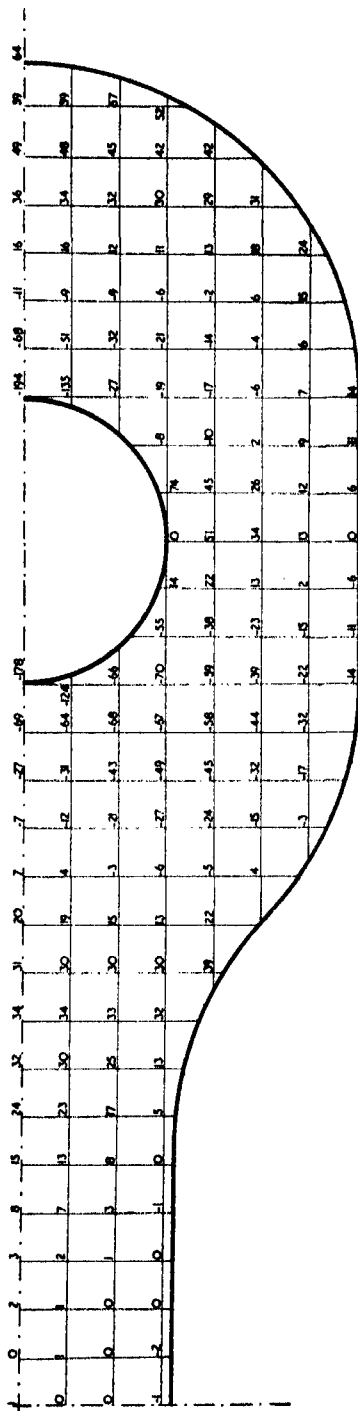


FIGURE 6d. (Y).

The relaxational solution

31. The problem now to be solved by Relaxation Methods is to determine χ by a use of the biharmonic 'pattern', permitting such additional (rigid-body) displacements of the internal boundaries (clamps) that each 'floats' freely under zero forces. When this problem has been solved, values of the three stress-components can be deduced; and in order to obtain the wanted stress-system it only remains to add the stresses previously deduced—namely, the stresses which are recorded in figures 5.

It is not necessary to explain the now standardized process whereby the relaxational solution was obtained. In figures 6, the first diagram (a) records the computed values of χ (including those which come from displacement of the floating clamps), the other three diagrams record the derived values of X_x , X_y and Y_y . These latter, which of course are subject to the unavoidable inaccuracies of a method based on finite differences, are in general smaller than the deducted stresses (recorded in figures 5) which of course are exact. Consequently the final solution (obtained by superposition of the stresses from figures 5 and 6) though not exact may be regarded as of high accuracy.

The final solution

32. This final solution is presented in figure 7, by nodal values and contours of the *principal stress-difference*, a quantity calculable from the formula

$$p_1 - p_2 = \sqrt{\{(X_x - Y_y)^2 + 4X_y^2\}}, \quad (51)$$

in which X_x , X_y , Y_y are to be given their values in the final (superposed) solution. The directions (ϕ) of the principal stresses—exhibited in their figure 6.182 by Coker & Filon (1931)—could of course be calculated from the formula*

$$\tan 2\phi = 2X_y/(X_x - Y_y), \quad (52)$$

but are not recorded here.

* The formulae (51) and (52) are derived (e.g.) in Southwell 1941, § 136.

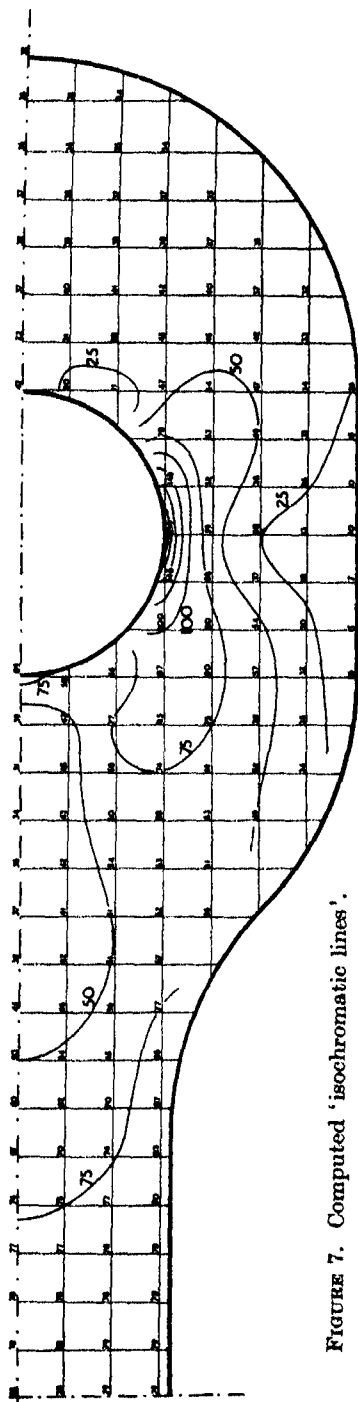


FIGURE 7. Computed 'isochromatic lines'.

CONCLUSION

33. Though some of its conclusions have been anticipated (e.g.) by Filon (1921), this general discussion of multiply-connected (perforated) plates is believed to be for the most part new. It had its origin in questions put to us by an engineer engaged in study of the stresses in the frames of locomotives. For theoretical estimates he had relied on Relaxation Methods, and had found these satisfactory; but Part VIIA gave no guidance in regard to the treatment of 'lightening holes' (cut with the aim of saving weight), and lacking guidance he had been compelled to neglect the holes. He believed that no great error had resulted; but now, having arrived at tentative conclusions, he desired to remove this source of uncertainty.

Initially it was suspected that allowance for holes, though feasible in theory, in practice would entail prohibitive labour. But on examination these fears proved groundless: so far from being prohibitive, the labour entailed by holes was seen to be quite small provided that their edges are not subjected to external tractions, fairly small provided that these tractions are self-equilibrating, and serious only in such problems as the example treated in this paper. These conclusions seemed sufficiently important to warrant publication, also some points remarked in the inquiry which appeared to have been generally overlooked: e.g. the possibility that solutions found by a use of Airy's stress-function may, in relation to multiply-connected (perforated) plates, be inadmissible for the reason that they (tacitly) presume 'self-straining'.

34. Those parts of the paper which deal with basic theory had been completed by the autumn of 1946, but publication had to wait for the numerical computations in Section VI. For these I am indebted to Miss E. D. Lang and to Miss G. Vaisey, also to the Clothworkers' Company for grants which made their collaboration possible in the summer of 1947. To Mr D. N. de G. Allen my thanks are due for his preparation of the diagrams and for much helpful advice.

Recently a paper has been published by R. D. Mindlin (1946) which also discusses the analogy between the equations for flexure ('slabs') and extension ('slices'), with special reference to perforations. It propounds integral relations which are confirmed by the conclusions of this paper; but I do not think it makes this paper superfluous, since it is not concerned with numerical computation. Mindlin contemplates a use of flexural experiments to determine extensional stresses: my own concern has been to show that the effects of holes can be determined *without* recourse to experiment.

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The limits of flame propagation at atmospheric pressure

I. The influence of 'promoters'

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The conditions for accurate determination of the limit mixtures for propagation of flame having been established, the effect of the addition of 0.5 % of such promoters and inhibitors as ethyl nitrate, diethyl peroxide, nitrogen peroxide, ozone, ether, acetaldehyde, ethyl alcohol and methyl iodide on the upper and lower limits of hydrogen-air, methane-air, *n*-butane-air (and propagas-air) mixtures was investigated. It is shown that the effects obtained are accounted for if the heat which the additive can contribute to the total heat available in the burning of the mixture is included. The only distinct promoting effect was that of ethyl nitrate on the upper limits of *n*-butane and propagas. Methyl iodide had a definite inhibiting effect except with hydrogen mixtures at the lower limit. The appearance of the flames has been carefully recorded as it gives some indication of the nature of the combustion process. The general inference is that pre-flame reactions have little influence on the limit mixtures, and that those mixtures are mainly determined by the heat available and consequently the temperature of the flame; inflammation being mainly caused by the radicals provided by the flame.

The limit mixtures of ethyl nitrate and nitrite were measured. The effect of replacement of oxygen by nitrous oxide on the hydrogen limits, and the effects of small additions of lead tetraethyl and of 0.5 % ethyl borate on *n*-butane limits are also noted.

1. INTRODUCTION

When mixtures of gases are too 'weak' in combustible they cease to propagate flame indefinitely, the flame dies out; when they are too 'rich', again the flame ceases to be propagated. Many investigations have been made on these lower and upper 'limit mixtures': the results of such investigations have been summarized by Coward & Jones (1928) and the summary has been revised by them more recently (1938). One object of the present work was to establish whether or not the composition of limit mixtures would be considerably affected by the addition of small quantities of other substances, 'promoters' or 'inhibitors' of combustion. When large quantities of fuel have to be burnt completely and rapidly in as small a space as possible (as, for instance, in the combustion chambers of turbo-jet engines) the addition of substances hastening the combustion might be beneficial, and if the limits of combustion were widened, the combustion might be more complete. A more fundamental object of the work however was to discover more about the reactions which lead to inflammation in a flame front; at the limits the flame speeds are slow and if reactions occur prior to inflammation they may be influenced by 'promoters'. The current view of flame propagation is not that ignition occurs in the unburnt gas owing to the heat conduction from the flame, but that a certain critical number of reaction centres giving rise to a minimum rate of reaction must be formed in the flame front. Townend (1939), for instance, suggests

that 'promoters' might therefore have a considerable influence, particularly for limit mixtures. The outcome of this investigation, however, has been to show that the limits of propagation are mainly governed by the temperature of the flame and not to a marked extent by pre-flame reactions. No real advantages are to be derived by the addition of so-called 'promoters', so far as limit mixtures are concerned.

The investigation divides itself into two parts: part I deals with the effect of small additions of different substances on the limit mixture compositions for several combustible gases, and part II with the influence of the physical properties of mixtures on the limits. An upper limit will be referred to as 'u.l.' and a lower limit as 'l.l.'.

2. EXPERIMENTAL

(a) General conditions for limit determinations

The considerable discrepancies in the recorded data of limit mixtures are due in part to the different conditions in which the measurements were made. It is well known that below a certain diameter, the cooling effect of the wall of the tube influences the composition of the mixture which will propagate flame. The tubes must, therefore, be wide enough for this effect to be negligible. They must also be long enough to permit the products to cool behind the flame front, and to allow the criterion of continued propagation to be ascertained. White (1924) has shown that, for most mixtures, the wall effect is very small above 5 cm. tube diameter and that a length of about 1.5 to 2 m. is sufficient. The mode of ignition makes some difference, but a naked coal-gas flame (1 in. jet of flame) drawn across the open end at the same time as the base plate is carefully slid away is usually satisfactory: the other end of the tube is kept closed. The direction of propagation influences the limits and must always be stated, for it is not possible to avoid entirely the effects of convection. In upward propagation the reduction in density in the flame front tends to favour propagation, the reverse is true for downward propagation, horizontal propagation being intermediate with an unsymmetrical flame front. Upward propagation gives better flame stability and consequently greater accuracy in limit determinations. Initial temperature influences the combustion limits, but room-temperature changes of a few degrees are insufficient to affect the results appreciably. The presence of water vapour may also influence the results, particularly with mixtures containing carbon monoxide, therefore the state of dryness of the mixture should be stated.

(b) Experimental details

The limits for upward propagation were determined in a vertical pyrex glass tube approximately 1.5 m. long and internal diameter 5.3 cm. The leads to manometer, gas storage vessels, oil pump, etc., entered through a cork which closed the tube at the top. This was rendered vacuum-tight with a coating of picene wax.

The bottom end of the tube was fitted with a brass cap which did not constrict the mouth of the tube and was closed by a ground brass plate (figure 1).

The gas mixtures were prepared in the tube by evacuating and admitting each component to the required partial pressure as measured by the manometer. The small quantities of promoter vapour (0.5 % of the total volume of the mixture) were first withdrawn from a small reservoir of the liquid into the evacuated tube. Room temperatures were $18 \pm 2^\circ \text{C}$; and all mixtures were dried over calcium chloride.

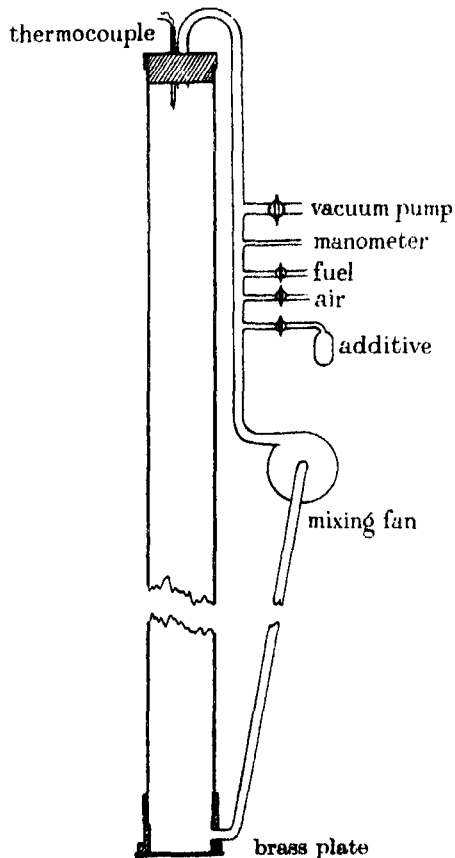


FIGURE 1

In order to mix the gases rapidly a small high-speed, vacuum-tight circulating fan of the centrifugal type was connected by 1 cm. bore glass tubes to the extremities of the combustion tube. The shaft of the fan was tightly packed with asbestos mixed with a non-volatile graphite grease. Although the top of the tube was strictly not a 'closed end', the limited size of the vent, representing only about 3.5 % of the end area, together with the resistance in the leads and fan, prevented any appreciable flow of gas from the top of the tube during a combustion.

A small 1 in. jet of burning coal-gas provided the source of ignition at the lower (open) end. The limiting concentration of a fuel in air for complete propagation throughout the tube was the mean value of the concentration (in percentage by volume of the gas in air) of the two mixtures, one which just completed combustion and one which just failed. On average, about twenty combustions were used to determine and check each limit. The error given in the tables which follow in the text, represents the reproducibility of the results under these experimental conditions. The concentration of promoters was maintained at 0.5% by volume in all the experiments; no attempt has been made to study the influence of the variation of their concentration.

(c) Preliminary experiments with propagas-air

It was convenient to start the investigation by making a preliminary survey of the effects of various substances upon the limits of inflammability of a sample of propagas.*

The effect of 0.5% by volume of the following additives was tried:

Diethylperoxide, because of its pronounced 'proknock' effect in concentrations as low as 10^{-4} mol. and because of the detection of peroxides in slow combustion products and even in flames. It was prepared by Baeyer & Villiger's method. b.p. 58 to 59.7° C (625 mm.).

Ethyl nitrate (B.D.H. 'pure') because of its similar 'proknock' effect and its probable dissociation to C_2H_5O radicals, similarly to ethyl nitrite.

Nitrogen peroxide, because it is a non-combustible peroxide with pronounced effect in lowering ignition temperatures.

Acetaldehyde, because it diminishes the ignition lag of hydrocarbons.

Ether, for comparison with diethylperoxide.

Ethyl alcohol, for general comparison.

(i) Results

The limits of propagation obtained expressed in percentage by volume of propagas in propagas-air mixtures are tabulated in table 1.

All the additives lower the l.l. but, as this is expressed in terms of propagas only, no conclusions regarding possible catalytic effects should be drawn since the addition of any combustible material would be expected to reduce the amount of propagas required in the limit mixture. The nitrogen peroxide does not contribute in this way and the reduction of the limit from 2.55 to 2.41% propagas might therefore be ascribed to a catalytic influence. Ethyl nitrate clearly has effect on the u.l., which is raised in spite of the increase in combustible material due to the promoter itself. Nitrogen peroxide also increases the u.l. slightly.

The alteration of the limits may be due to two separate influences (a) an increase in the combustible material, and (b) a further catalytic combustion-promoting

* See footnote to table 1.

activity. The two influences may be considered to be supporting each other towards the l.l. and opposing each other at the u.l. Conclusions to be drawn from the above results will be discussed later in §3.

TABLE 1

promoter	l.l.	u.l.
propagas† alone	2.55	9.6
(C ₂ H ₅) ₂ O ₂ (0.7 %)	1.72	9.7
(C ₂ H ₅) ₂ O (0.5 %)	2.03	9.2
C ₂ H ₅ ONO ₂ (0.5 %)	2.22	12.4
C ₂ H ₅ OH (0.5 %)	2.31	9.3
NO ₂ (0.5 %)	2.41	9.8
CH ₃ CHO (0.5 %)	2.14	9.5
limits of error	± 0.04	± 0.1
† Propagas: C ₄ hydrocarbons trace		
C ₃ hydrocarbons 96 %		
C ₄ hydrocarbons 4 %		
96 % saturated.		

(ii) *Description of the appearance of the flames*

There are considerable differences in the appearance of the flames; it is important to record differences as they provide information about the chemical and physical changes which occur, but the appearance of the propagas flames were similar to those obtained in butane mixtures which are described later (see p. 181).

(d) *Hydrogen-air*

The preliminary experiments with propagas mixtures were followed by a careful measurement of the effect of the same additives on limit mixtures of hydrogen, methane, and butane with air all under similar conditions.

The normal limits of inflammability of hydrogen in air were determined first for comparison with values found in the literature, which are many and varied and depend upon the conditions in which the measurements were made. Complete darkness was essential for observation of the flames which are only weakly luminous. At the l.l. the flame front tends to break into 'pockets' of combustion, and these have to be distinguished from flame caps which rise, diminishing, through the tube in mixtures of weaker composition than that of the lower limiting value. The criterion for indefinite propagation was that the 'pockets' of flame should all be contained in an area normally occupied by a uniform flame front (as opposed to burning individually and irregularly through the gas) and that they should not diminish as they progressed up the tube.

In tubes of 5 cm. diameter, White (1924) gives the l.l. for upward propagation as 4.15. Coward & Jones (1928) quote 4.1 ± 0.1 , Coward & Brinsley (1914) made many observations in still wider tubes (limit 4.1) and discussed the above criterion for certifying the limit. For the u.l. for upward propagation, Coward & Jones quote 74 ± 0.5 ; White (1924), 74.5.

In addition to the substances already mentioned, ozone, which has been found to be a strong proknock, was included as a promoter, and methyl iodide as an inhibitor. Ozone has been supposed to be a chain carrier in CO oxidation by Lewis & von Elbe (1937); methyl iodide suppresses explosive and slow oxidation of hydrocarbons, carbon monoxide and hydrogen, by removing hydrogen atoms and other free radicals.

For ozone a modification of the apparatus was, of course, necessary. As far as possible glass was used throughout and both ends of the tube were protected by hard paraffin wax. The metal fan box had to be eliminated, mixing being effected by rocking a glass sphere up and down the tube.

The ozone was prepared by passing oxygen, dried over P_2O_5 , through a powerful silent discharge across the annular space in a Berthelot tube and was stored over concentrated sulphuric acid in a glass gasholder. Decomposition in the storage vessel was quite slow, approximately 10% of the ozone decomposing in 24 hr. The dilute ozone was analyzed immediately before use and the appropriate amount of oxygen-ozone mixture introduced into the combustion tube. Oxygen and nitrogen were added to bring the gases in the tube, apart from the fuel, to the composition of air, the ozone being considered as oxygen. Experiments were carried out to determine the maximum amount of ozone decomposed in the gas leads and combustion tube before ignition. For l.l. concentrations decomposition was found to be between 5 and 6% of the ozone. For 1 min. delay in igniting the mixture, decomposition increased to about 12%, for 5 min. delay to 17%. The concentration of ozone needed to introduce 0.5% of the total volume of the mixture into the u.l. hydrogen mixtures was higher than could be conveniently obtained.

(i) Results

The results for the limits of propagation for hydrogen mixtures are summarized in table 2.

TABLE 2

promoter	% vol. H_2	
	l.l.	u.l.
hydrogen alone*	4.19	74.6
$(C_2H_5)_2O_2$ (0.5%)	3.82	68.5
$C_2H_5ONO_2$ (0.5%)	3.92	70.9
NO_2 (0.2%)	4.15	73.7
NO_2 (0.5%)	4.10	72.9
NO_2 (0.9%)	4.18	71.7
CH_3I (0.5%)	4.19	61.3
O_3 (0.4%)	3.92	—
limits of error	± 0.04	± 0.3

* (99.5% H_2 , the remainder for the most part nitrogen.)

Diethyl peroxide and ethyl nitrate reduce both the upper and lower limits, a behaviour compatible with the mere addition of extra combustible material. Increasing quantities of NO_2 lower the u.l. proportionally, but a linear relationship

is not obtained at the l.l. These l.l. figures for NO_2 differ by very little from the normal value. The effect of methyl iodide appeared to be confined to the upper limit.

(ii) *Description of the appearance of the flames*

The l.l. flames without additives were barely visible and pale blue in colour. The flames towards the upper limit were considerably faster. They were also slightly more luminous. The appearance of the flames was not altered radically by the additives (except methyl iodide), but colour changes were observed and the flames were more luminous.

Ethyl nitrate and nitrogen peroxide imparted the usual yellow-green coloration to the flames towards the l.l., but those near the u.l. consisted of a blue flame front with the addition of a grey-green tail: the absence of oxygen atoms in the flame of the rich mixture is indicated, cf. Gaydon (1944). It was particularly noticeable with ethyl nitrate that the l.l. flames no longer burned in 'pockets'. With a decrease of hydrogen content from 4.0 to 3.7 % approximately (+ 0.5 % ethyl nitrate), the size of the flame decreased proportionally from almost filling the diameter of the tube to a small hemispherical flame, about $\frac{3}{4}$ in. in diameter, rising up the centre of the tube. The limit for indefinite propagation was rather difficult to judge; 3.9₂ % was decided as the likely minimum percentage. A vibratory motion of the flame attended nitrogen peroxide additions to u.l. mixtures.

The change of flame character was most pronounced in the case of methyl iodide. Above 5 % hydrogen (+ 0.5 % methyl iodide) a coherent flame front was observed consisting of multicoloured streaks and elongated pockets of flame, the predominant colours being orange and green. These became individual pockets and diminished in size and number with a decrease in hydrogen concentration until the limit was reached, when they began to burn independently throughout the gas. The flames near the u.l. in the presence of methyl iodide (the limit was lowered considerably) were noisy owing to the resonance of the rapid vibrations of the flame front, and consisted of a blue flame front with a long conical orange tail. A long tail can be either indicative of a slow after-burning or of a slow cooling of radiating products. Hydrogen iodide and iodine were liberated in both the flames.

(iii) *Limits of nitrous oxide-hydrogen mixtures*

Replacement of the oxygen in the air by an equal volume of nitrous oxide was found to have no effect on the position of the l.l., although the u.l. was reduced far beyond the point expected as a result of halving the oxygen content of the system (i.e. 1 mol. N_2O replacing 1 mol. O_2). Doubling the N_2O percentage only brought the u.l. to 65.8 % hydrogen and narrowed the l.l. to a small extent.

TABLE 3

	l.l.	u.l.
hydrogen and air	4.19	74.6
hydrogen and air [21 % N_2O + 79 % N_2]	4.19	29.0
hydrogen and air [42 % N_2O + 58 % N_2]	4.38	65.8

The l.l. flames were very similar in appearance to the normal hydrogen flames. The flames towards the u.l. had an unusual and very definite structure. The hemispherical front was blue and followed by a conical orange glowing tail. They were very much slower than the normal u.l. hydrogen flames.

(e) *Methane-air*

The study of the combustion of limit mixtures commenced in Davy's time with measurements made on methane mixtures; ever since then numerous measurements have been made on such mixtures, but the results were very discrepant until Coward established the conditions necessary for concordance. The mean of the best values in the literature for the limits in a 5 cm. tube for upward propagation are 5.3 to 14.3; (Coward & Brinsley (1914) obtained for the l.l. 5.32 for a 10 in. cylindrical tube 7 ft. long.)

(i) *Results*

The effect of additives was similar to that obtained with the hydrogen-air system with two exceptions: (a) *nitrogen peroxide* raised the u.l. from 14.3 to 14.9%. The u.l. of hydrogen was progressively lowered by increasing NO_2 additions; (b) *methyl iodide* raised the l.l. from 5.26 to 6.29%, whereas the hydrogen l.l. was unaffected by methyl iodide. The results are given in table 4.

TABLE 4

promoter	l.l.	u.l.
methane alone*	5.26	14.3
$(\text{C}_2\text{H}_5)_2\text{O}_2$ (0.5%)	4.16	13.9
$(\text{C}_2\text{H}_5)\text{ONO}_2$ (0.5%)	4.47	14.1
NO_2 (0.5%)	4.93	14.9
O_3 (0.4%)	5.07	14.5
$(\text{C}_2\text{H}_5)_2\text{O}$ (0.5%)	4.02	13.4
$\text{C}_2\text{H}_5\text{OH}$ (0.5%)	4.54	---
CH_3I (0.5%)	6.29	12.3
limits of error	± 0.04	± 0.1

* Analysis: 99% CH_4 , remainder air.

(ii) *Description of the appearance of the flames*

The normal methane flames towards the l.l. were blue hemispherical shells, not very definitely shaped. They did not quite touch the walls of the vessel and no tail was visible.

The u.l. flames were longer and more definite in shape. A faint dark-red glowing tail, fairly short, was visible. As the mixture strength approached the theoretical value for complete combustion, the flames acquired the usual green tinge, indicating Swan bands, and the tail became more obvious.

One striking difference was noted in the character of the l.l. flames of methane with ethyl nitrate or nitrogen peroxide. As the l.l. was approached, the flame no longer assumed its usual form, but became more diffuse and burnt in a long column

which progressed up the tube. The absence of a definite flame front was conspicuous. This occurred to a lesser degree at the u.l. The characteristic emission from the reaction $\text{NO} + \text{O} \rightleftharpoons \text{NO}_2 + h\nu$ was apparent in both instances. No secondary reaction emitting visible light was noticed behind the flame fronts of methane or hydrogen flames in the presence of ethyl nitrate or nitrogen peroxide, whereas with propane and butane this was plainly visible. If the glow is due to hot NO_2 , the flame temperatures of limit mixtures of both methane and hydrogen must be considerably less than those of propane and butane. In the presence of methyl iodide the l.l. flames consisted of a blue-green flame front followed by a long conical orange glow.

(f) *n*-Butane-air

n-Butane was next chosen for study, being typical of the higher normal hydrocarbons in its combustion behaviour. For 5 cm. tubes, the limits for upward propagation (1.86 to 8.41) were given by Coward, Jones, Dunkel & Hess (1926).

A sample of pure *n*-butane was obtained by fractionation of a commercial material in a specially constructed column. The *n*-butane boiling from 0 to 1.5° C was collected and stored in a small cylinder.

(i) *Results*

The limits of combustion of the *n*-butane with air in the 5.3 cm. tube were found to be 1.93 to 9.05 % (upward propagation).

TABLE 5

promoter	% vol. butane	
	l.l.	u.l.
<i>n</i> -butane alone	1.93	9.05
$(\text{C}_2\text{H}_5)_2\text{O}_2$ (0.51 %)	1.45	9.18
$\text{C}_2\text{H}_5\text{ONO}_2$ (0.50 %)	1.62	12.3
NO_2 (0.50 %)	1.96	9.75
H_3CNO_2 (0.50 %)	1.82	9.86
$(\text{C}_2\text{H}_5)_2\text{O}$ (0.50 %)	1.46	8.88
CH_3CHO (0.50 %)	1.73	9.08
CH_3I (0.50 %)	2.11	6.20
$\text{B}(\text{OC}_2\text{H}_5)_3$ (0.50 %)	1.47	8.5
$\text{Pb}(\text{C}_2\text{H}_5)_4$ (trace)	2.00	8.87
Ph.NHCH_3 (trace)	1.87	8.91
limits of error	± 0.03	± 0.05

Diethyl peroxide depressed the l.l., but not more than would be expected from the addition of extra combustible (see later). The u.l. was raised more than is obvious since the equivalent u.l. of the mixture reckoned as butane would have been 9.63.

Ethyl nitrate did not lower the l.l. quite as much as diethyl peroxide but the rise in the u.l. was considerably greater. This effect does not appear to be due to *nitrogen peroxide* liberated, because addition of the latter has only a small effect on the u.l. and hardly any on the l.l.

Nitromethane (which probably dissociates into CH_3 and NO_2) has much less effect than ethyl nitrate, but a rather greater effect on the u.l. than nitrogen peroxide when allowance is made for the addition of combustible.

Ether has about the same effect as ethyl peroxide on the l.l., but an effect in the opposite direction on the u.l.

Acetaldehyde had only a small effect.

Ethyl borate had no real promoting effects (see p. 188).

Lead tetraethyl could only be introduced as a trace (about 0.0003 %) since its v.p. at 17° C is only 0.216 mm., but both limits were slightly inhibited.

Summarizing the apparent effects of these additions on the combustion limits of butane recorded in table 5, ethyl peroxide and ethyl nitrate widen the combustion range at both limits, ether at the l.l. only, NO_2 and nitromethane at the u.l. only, while methyl iodide narrowed both, particularly the u.l. However, as will be shown later, allowing for the thermal effect of the additives, catalytic influences seem to be confined to the u.l.

(ii) *Description of the appearance of the flames*

The butane flames towards the l.l. were blue hemispherical shells filling the diameter of the tube completely. (Methane and hydrogen l.l. flames did not reach the walls of the tube.) The u.l. flames were of quite a different character being longer, less luminous and not touching the walls. Slightly less rich u.l. mixtures showed in the centre part of the flame yellow-white luminosity due to incandescent carbon particles.

Diethyl peroxide did not change the l.l. flames near the limit, but mixtures richer than 1.68 % easily acquired a vibratory character ending in mild explosion. In spite of the greater heat of combustion of butane itself, an equal volume of butane did not give rise to such a fierce burning mixture. A dark reddish tail to the flame was noticed in mixtures just above the l.l., but this showed itself even when diethyl peroxide was not present. The u.l. mixtures with diethyl peroxide were not visibly different from those without the addition.

Ethyl nitrate gave bright cream coloured l.l. flames tinged pale green at the rim touching the tube walls and followed by an orange glowing tail. The u.l. flames were increased in length; the definite flame front was lost and a column of flame moved up the centre part of the tube. Mixtures of about 10.4 % butane with 0.5 % ethyl nitrate were indistinguishable from the butane flames alone, the absence of the characteristic NO_2 coloration was conspicuous. As the percentage of butane was increased, the carbon luminosity in the centre decreased and a faint NO_2 coloration could be observed. Oxygen atoms cannot therefore be playing an important role in this u.l. combustion. These weak flames continued to burn in mixtures beyond the normal u.l. in spite of the increased fuel concentration due to the ethyl nitrate.

The change in flame character produced by *nitrogen peroxide* and *nitromethane* was the same as with ethyl nitrate and so this may be attributed entirely to NO_2 ; no NO oxidation coloration was observed in the u.l. flames, but only at the l.l.

The addition of *ether* and *acetaldehyde* did not change the appearance of the flames.

The addition of *methyl iodide* gave a creamy blue l.l. flame front with a long deep orange tail. The u.l. flames were unusual in shape having a green tinged front with a blue rim tailing off into a reddish glow at the base of the flame.

Ethyl borate caused l.l. flames to be tinged an intense green and were otherwise like those to which methyl iodide had been added. The u.l. flames were unchanged by the addition.

Lead tetraethyl coloured the l.l. flames grey-blue and provided a long greenish white tail. The u.l. flames were again unchanged in appearance.

(g) *Lower limits of ethyl nitrate and ethyl nitrite*

The l.l. mixtures of these substances by themselves, as quoted from the literature, are discrepant:

Lower limit of ethyl nitrate 3.8 % (Le Chatelier & Boudouard 1898).

Lower limit of ethyl nitrite 3.01 % (A. G. White 1922).

The l.l. of these two substances were therefore redetermined and found to be:

4.00 % (± 0.03) for ethyl nitrate (b.p. 87°C).

4.11 % (± 0.03) for ethyl nitrite (b.p. 17 to 18°C).

The quite small difference found in the limits is compatible with their minor structural differences.

The flames of both these compounds were similar in appearance to those of lower limit butane mixtures containing ethyl nitrate but the colorations were somewhat more intense.

3. INTERPRETATION OF THE EXPERIMENTAL RESULTS

The quotation of limits, in terms of percentage by volume of the fuel only, does not truly reveal the catalytic influences that may be operative because of the contribution made by some of the additives to the total fuel content. The effectiveness of a non-combustible promoter is immediately apparent from the limit figures, but if it is itself inflammable, then any combustion promoting or inhibiting influences are masked. At the l.l. all positive effects with combustible promoters would be confused, and at the u.l. all but the more powerful effects, where the limit is raised in spite of the increase in fuel concentration, would be concealed. For instance, the u.l. in presence of the promoter may be lower than the normal limit, yet a higher percentage of total combustible may be present. A basis for comparison of the mixtures is required in which the two factors—catalysis and change of fuel concentration—may be distinguished.

The usual basis for comparison is to establish whether the mixture obeys Le Chatelier's rule that 'all mixtures of limit mixtures are limit mixtures'. This rule has been put to the test over a wide variety of substances. Le Chatelier & Boudouard (1898) showed that it held for mixtures of acetylene and carbon monoxide which have very different combustion characteristics. Coward, Carpenter & Payman (1919) using *upward* propagation showed that it held approximately

for upper and lower limit mixtures of hydrogen, carbon monoxide and methane. White (1922) made an extensive investigation and showed that the rule held for many vapour mixtures at both limits, but not always for upward propagation at the u.l.; also when substances present in the mixture gave rise to cool flames, then the rule did not hold.

It is rather remarkable that the rule is so comprehensive: it seems that the combustion mechanism belonging to a substance which influences the slow combustion or ignition behaviour of another combustible substance, must be having very little effect on limit mixtures of such substances. Le Chatelier & Boudouard (1898), Burgess & Wheeler (1911) and particularly White (1924) have all drawn attention to the fact that the combustion heat per mol. of limit mixture is nearly constant for many different mixtures, and this fact is the significant one in seeking an explanation of the wide application of Le Chatelier's rule.

It would have been possible to test the application of Le Chatelier's rule in the case of the additives here used, but the quantities added were small and the limits of the individual additives were not always available. It was, therefore, preferable to find the change in the total combustion heat due to the presence of the compound added. The total heat of combustion of a mixture, although it may not be fully operative, is the main factor controlling the limits and is taken as a measure of the amount of fuel present in any mixture and provides a means for comparison. The two limits will be dealt with separately.

(i) *Lower limit mixtures*

Table 6 gives the calorific values of all the l.l. mixtures investigated in this work; a lower figure for the complex mixture than for the fuel alone indicates a promoting influence on the part of the additive.

TABLE 6. LOWER LIMIT MIXTURES

l.l. mixture*	net calorific value (kcal./mol.)	l.l. mixture*	net calorific value (kcal./mol.)
hydrogen	2.42	propagas	11.29
+ (C ₂ H ₅) ₂ O ₂	5.38	+ (C ₂ H ₅) ₂ O ₂	11.56
+ C ₂ H ₅ ONO ₂	3.80	+ C ₂ H ₅ ONO ₂	11.30
+ NO ₂	2.40	+ NO ₂	10.67
+ O ₂	2.42	+ (C ₂ H ₅) ₂ O	12.02
+ CH ₃ I	3.46	+ C ₂ H ₅ OH	11.75
		+ CH ₃ CHO	10.77
methane	10.04	butane	12.26
+ (C ₂ H ₅) ₂ O ₂	11.07	+ (C ₂ H ₅) ₂ O ₂	12.27
+ C ₂ H ₅ ONO ₂	10.09	+ C ₂ H ₅ ONO ₂	11.77
+ NO ₂	9.42	+ NO ₂	12.44
+ O ₂	9.86	+ (C ₂ H ₅) ₂ O	12.32
+ (C ₂ H ₅) ₂ O	10.85	+ H ₃ C.NO ₂	12.37
+ C ₂ H ₅ OH	10.30	+ CH ₃ CHO	12.29
+ CH ₃ I	12.92	+ CH ₃ I	14.32

* Composition given in previous tables.

Figure 2 is obtained by plotting the values of the heat of combustion of the limit mixtures against the reciprocals of the l.l. and drawing as a reference line a curve through CO and the now fairly well established values of the normal hydrocarbons up to *n*-butane (see part II, pp. 193, 202). The graph gives a means of testing the influence of any promoters or inhibitors, because the 0.5% additions would have

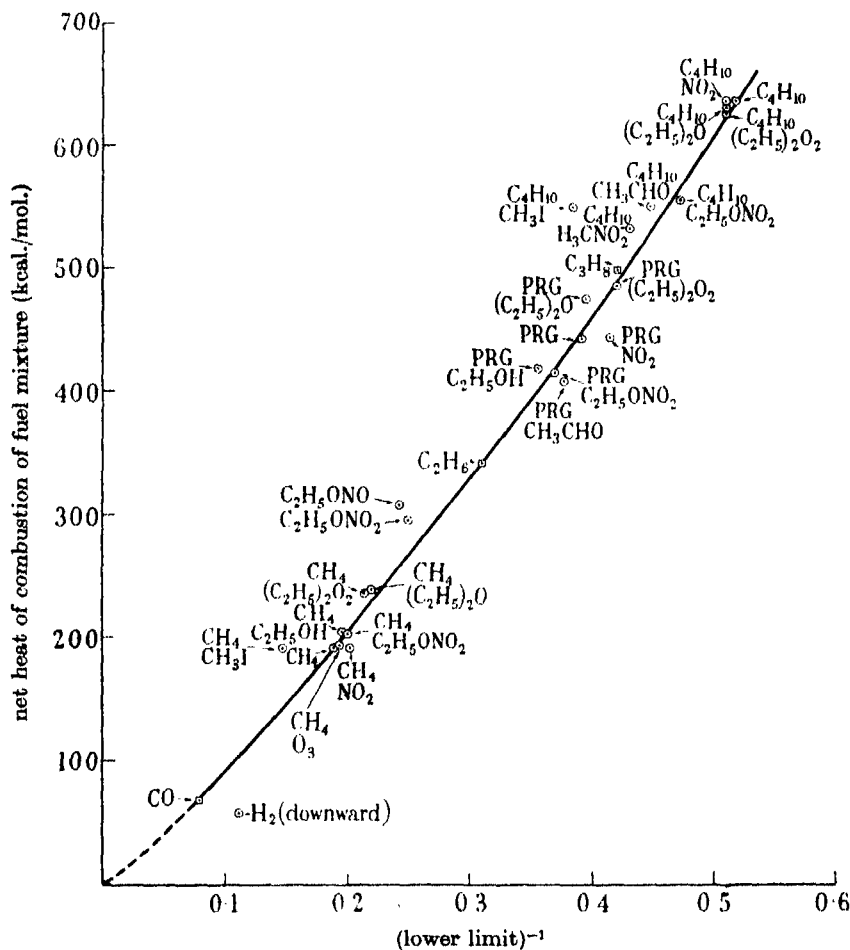
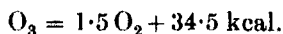


FIGURE 2. PRG = propagas, $\square$ = figures from literature.

no appreciable effect on the physical properties of the mixture, and any departure outside the experimental error from the line drawn through the values for the hydrocarbons would indicate a specific effect on the reaction mechanism. Those mixtures corresponding to points which lie to the right of the line may be considered as burning with greater readiness than those to the left, since they propagate flame in mixtures with less heat available.

The graph reveals that there are no important catalytic effects at the l.l. Some minor positive effects are apparent, notably with nitrogen peroxide, but some of the additives, in spite of their positive influences on ignition and knock, tend to inhibit slightly rather than promote. This was contrary to expectation, since the presence of potentially active centres from organic peroxides, nitrates, etc. in the heated gas ahead of the flame might have been expected to increase the number of chains started and facilitate combustion. The negative effects are not large except with methyl iodide and all points lie quite close to the reference curve. It appears therefore that the principal factor governing flame propagation towards the lower limit of inflammability is the heat available in the mixture.

The effect of ozone is also interpreted thermally. It is assumed to decompose in the flames which already contain excess oxygen and a high proportion of diluent nitrogen, according to



The heats of combustion of the mixtures containing O_3 were calculated on this basis, and for the methane mixture the point lies directly on the reference curve.

Minor influences of the promoters on the l.l. as detailed in the following three paragraphs are noticeable, although in the main there is little effect.

In the methane mixtures the peroxide behaved very similarly to ether, both slightly inhibiting the reaction. Ethyl nitrate appeared to have a very slight promoting influence, but when it is considered that nitrogen peroxide alone had a greater effect, no positive activity could be attributed to the ester itself.

With propagas as the fuel, the behaviour of ether and diethyl peroxide was no longer similar; whereas the ether seemed to inhibit the reaction slightly, the peroxide had but little effect. The ethyl nitrate again appeared to have but a slight positive influence, which was small in comparison with that of nitrogen peroxide.

In the butane system only the ethyl nitrate had a small promoting influence. Nitrogen peroxide appeared to have a small opposite effect here, so the activity of the ethyl nitrate cannot in this instance be attributed to this part of the molecule.

The figures obtained with hydrogen mixtures are not included on the graph. The behaviour of hydrogen in upward propagation is quite exceptional; the flame is propagated very readily. Goldman (1929) has explained the peculiar mode of the upward flame propagation in l.l. hydrogen flames by showing that the combustion is maintained in small rising regions of burning gas by diffusion of the hydrogen, in preference to other gases, into those centres of activity; thus the flame is maintained with quite a low percentage of hydrogen in the mixture. For downward propagation, the limit is 9.0%, and this figure would be more in keeping with the figures used for other gases, as there is only a small difference between upward and downward limit compositions for the hydrocarbons. Nevertheless, though nearer, this would also be somewhat off the curve (figure 2). The figures in table 6, however, show that the effect of the additives is mainly thermal, and that no promoting effects are obtained, except a very slight effect with nitrogen peroxide.

There is no inhibiting effect of methyl iodide on the l.l. of hydrogen, although it has a marked effect on the appearance of the flame.

(ii) *Upper limit mixtures*

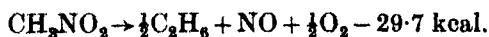
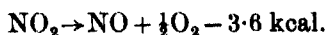
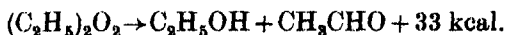
There is much more uncertainty in ascertaining the real effect of the additives on the upper limits; although all the oxygen is consumed, it is not found in the products entirely as carbon dioxide and water. A rather crude estimate of the effect of promoters on u.l. mixtures may be made by finding the heat theoretically available from the mixtures, compared with that from the fuel-air mixtures without additives. A promoting influence is then detected by a figure smaller than that for the fuel alone, indicating that flame is propagated in the mixture although less heat is liberated per unit volume.

The heat of reaction in kcal./mol. of the limit mixture is obtained assuming that all the oxygen in the very rich mixture is consumed.

The fraction:

$$\frac{(\% \text{ O}_2) \times (\text{net heat of combustion of fuel/mol.})}{(\text{no. of O}_2 \text{ mol. for complete combustion of 1 fuel mol.}) \times 100}$$

does not represent the actual amount of heat evolved, for all the oxygen is not burnt to $\text{CO}_2 + \text{H}_2\text{O}$, but it can be used for comparison of effect when the quantity of additive is small. The two columns of figures in table 7 give the available heat estimated in two ways. The first is based upon the free oxygen content of the mixtures; the second column shows the heats allowing for the dissociation of the promoter to simple products stable in rich mixtures. Any oxygen liberated during the decomposition is considered to be consumed by the hydrocarbon. The amount of heat summated in this way gives a rough figure for comparison with other mixtures. The assumed decompositions are:



The upper limit mixtures of *hydrogen* have shown no instance of positive catalysis; in fact, all the additions appear to inhibit the reaction. Increasing additions of nitrogen peroxide progressively lower the limiting concentration, although considerably more heat than would be required to dissociate the nitrogen peroxide is available in the mixture. The absence of the characteristic emission of



appears to indicate that inhibition is not due to this reaction. The figures in table 7 show that the reduction of hydrogen in the rich mixture is greater than that required to compensate for the reduction in free oxygen content due to the additive.

The effects of the promoters on the methane upper limit are small and indefinite. The heat available in mixtures containing diethyl peroxide and ethyl nitrate is less than normal if calculated on a free oxygen basis, but taking into account decomposition of the promoter, a similar or greater amount of heat is required for

TABLE 7

		net heat available	
			assuming
		on free O ₂ basis;	decomposition of
		kcal./mol.	the promoter;
mixture		of mixture	kcal./mol.
			of mixture
hydrogen			
74.6 %		6.18	—
73.7 + 0.2 %	NO ₂	6.31	6.42
72.9 + 0.5 %	NO ₂	6.45	6.68
71.7 + 0.9 %	NO ₂	6.65	7.06
68.5 + 0.5 %	(C ₂ H ₅) ₂ O ₂	7.53	7.69
70.9 + 0.5 %	(C ₂ H ₅)ONO ₂	6.95	7.00
61.3 + 0.5 %	CH ₃ I	9.28	—
methane			
14.3 %		17.2	—
13.9 + 0.5 %	(C ₂ H ₅) ₂ O ₂	17.17	17.34
14.1 + 0.5 %	C ₂ H ₅ ONO ₂	17.12	17.16
14.9 + 0.5 %	NO ₂	16.96	17.14
14.5 + 0.4 %	O ₃	—	17.40
13.4 + 0.5 %	(C ₂ H ₅) ₂ O	17.26	—
12.3 + 0.5 %	CH ₃ I	17.5	—
propagas			
9.6 %		16.8	—
9.7 + 0.6 %	(C ₂ H ₅) ₂ O ₂	16.67	16.98
12.4 + 0.5 %	C ₂ H ₅ ONO ₂	16.18	16.21
9.8 + 0.5 %	NO ₂	16.68	16.34
9.2 + 0.5 %	(C ₂ H ₅) ₂ O	16.78	—
9.3 + 0.5 %	C ₂ H ₅ OH	16.76	—
butane			
9.05 %		18.66	—
9.18 + 0.5 %	(C ₂ H ₅) ₂ O ₂	18.52	18.69
12.3 + 0.5 %	C ₂ H ₅ ONO ₂	18.10	18.56
9.75 + 0.5 %	NO ₂	18.41	18.6
9.86 + 0.5 %	H ₃ C. NO ₂	18.39	18.33
8.88 + 0.5 %	(C ₂ H ₅) ₂ O	18.59	—
9.06 + 0.5 %	CH ₃ CHO	18.53	—
6.20 + 0.5 %	CH ₃ I	19.16	—
8.5 + 0.5 %	B(OC ₂ H ₅) ₂	18.67	—

flame propagation in the mixture compared with the normal limit mixture. No significant positive catalysis appears to be present. The small increases due to nitrogen peroxide and ozone may be explained by the extra oxygen available from the promoter.

The *propagas* and *butane* systems are almost identical in their response to the promoters. Table 7 indicates that ethyl nitrate exerts a definite positive catalytic

influence on the u.l.'s, and that NO_2 and nitromethane have a somewhat similar effect. Diethyl peroxide and ether have no appreciable effect.

It is curious that ethyl nitrate appears to have effect and the peroxide little, if any. Its activity is probably not due to oxides of nitrogen, as NO_2 has been shown to have but a small promoting influence. The flames with the ethyl nitrate and peroxide additions did not have the same appearance.

An attempt to find out whether the activity of ethyl nitrate was due to ethoxy radicals was made by testing the effect of additions of triethyl borate. There was a lowering of the u.l., indicating inhibition if anything, but this might have been due to the boron-containing radicals overcompensating for any effects of the ethoxy radicals.

The observations of White & Price (1919) are relevant; they investigated the effect of diethyl peroxide and ethyl hydrogen peroxide on the limits of *ether-air* mixtures, and found that the l.l. was unaffected, but the u.l. (for downward propagation) was slightly raised when a considerable quantity of the peroxides was added. (The peroxides were counted as ether in the mixtures.)

Although large positive catalytic effects observed in this work have been limited to the effect of ethyl nitrate on the u.l. of the higher hydrocarbons, methyl iodide acted as an inhibitor with all the fuels. Both upper and lower limits were affected, except the hydrogen lower limit which, in terms of hydrogen, remained unchanged. The iodide was dissociated and no doubt the combustible part of the molecule was burnt, so even here the l.l. mixture was richer in fuel than usual. The inhibition is not entirely explained on the grounds that it abstracts heat from the system for its dissociation, or by its high specific heat. If this were so, the difference in the heat available in the limit mixtures with and without methyl iodide would be constant and independent of the fuel; table 7 shows that this is not so. The inhibiting action of methyl iodide is generally due to the removal of chain carriers such as alkyl radicals by the halogen which is the active part of the molecule. Flame speeds remain slow as the theoretical mixture is approached if methyl iodide is present, but the visible radiation increases in intensity and the length of the 'tail' radiating after passage of the flame front also increases. West & Miller (1940) have found evidence for a resonance transfer of energy from fluorescent hydrocarbons in solution to alkyl iodides, which suggests a similar deactivation in the gas phase of energy-rich hydrocarbon molecules essential to chain propagation.

Although such promoting effects as have been found on lower and upper limits have been small, the response to additives has tended to increase in the direction of the higher hydrocarbons.

(iii) *Discussion of the appearance of the flames*

The characteristics of the flames have been described carefully in §2.

All l.l. flames for upward propagation were of the same structure, consisting solely of thin blue hemispherical shells which remained unchanged by any of the

additives except methyl iodide and those compounds giving rise to nitrogen peroxide. The stability and tenacity of shape of the l.l. flames increased from hydrogen to butane.

It is clear that with hydrogen and methane when there is excess of oxygen, the reactions in the flame are not continued far behind the flame front, and that there is appreciable heat loss in the neighbourhood of the walls. With propane and butane, the flames are hotter, so there is no gap and the products of the additives are excited by the hotter products behind the flame.

The u.l. flames showed much more variation. Hydrogen flames were almost flat, and frequently vibratory. They completely filled the tube. Methane u.l. flames showed a tendency to elongate, the blue flame front becoming a paraboloid, followed by a short reddish conical tail. Propane and butane flames were quite unlike the l.l. flames; they were very long and the flame front was only faintly luminous, although the centre of the flames, especially just beneath the dome of the flame, showed the smoky yellow luminosity of incandescent carbon. The structures of the u.l. flames were on the whole more sensitive to the additives than the l.l. flames. It is significant that although there may be no influence on the limits, the presence of the additive often alters the flame characteristics (e.g. ethyl nitrate on hydrogen flames, see p. 178). The relation between the upper and lower limit flames is considered in part II.

4. CONCLUSION

It has been found that the presence of promoters in the gas ahead of the flame has little specific influence on the propagation limits. It is therefore probable that the main criterion for inflammation is the maintenance of a sufficient rate of reaction and heat release in the flame, providing thereby sufficient active radicals to inflame the entering gases. The appearance of the upper and lower limit flames show that, after inflammation occurs, the additives may influence the flame characteristics, particularly in the upper limit region. Only with methyl iodide (inhibitor) and ethyl nitrate (promoter) was there any indication of action prior to entry and even in those cases the action may be due to an influence on the rate of reaction in the flame and therefore on the flame boundary temperature. The conclusions of this work are in agreement with earlier work, particularly that of White (*loc. cit.*) who showed that there was no relation between limits for propagation of flame and ignition temperature as ordinarily determined. The particular reaction mechanisms determining ignition seem to have little connexion with the power to propagate flame.

Since the heat of combustion is the main factor determining the composition of the limit mixture, it was of importance to study the physical properties of limit mixtures, an extension of the investigation in this direction is described in part II, at the end of which acknowledgements are made.

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The limits of flame propagation at atmospheric pressure II. The influence of changes in the physical properties

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The effect of replacing the nitrogen of the air by other diluents, such as CO_2 , A and He, on the limits of propagation of flame in hydrogen and methane mixtures has been determined. The results indicate that the flame is only propagated if a certain minimum temperature can be maintained in the flame boundary, which is approximately constant for a given combustible. The specific heat of the mixture and heat of combustion of the combustible constituents determine whether the flame is propagated; differences of thermal conductivity are only great enough in hydrogen mixtures or in mixtures containing helium to have a pronounced influence.

It is possible to estimate the upper limits in oxygen from the value of the lower limit in air for mixtures which are completely burnt, but with the hydrocarbons which are not completely burnt to CO_2 such estimate cannot easily be made. The lower limits for *n*-pentane, *iso*-pentane, *n*-hexane, *n*-heptane, *n*-octane and 2, 2, 4-tri-methyl pentane have been carefully redetermined. The heat of combustion multiplied by the percentage of hydrocarbons in the lower limit mixture is not quite constant, but more heat is required to maintain the combustion of the higher hydrocarbons.

Other evidence is mentioned in support of the view that flame limits are determined by a certain minimum temperature representing a certain minimum reaction rate at the flame boundary, the flame being maintained, not by the pre-heating and consequent reaction of the mixture, but chiefly by radicals provided by the flame.

1. INTRODUCTION

It is obviously an important problem in combustion chemistry to ascertain the particular properties of a gaseous mixture which determine whether or not it will propagate flame. Le Chatelier & Boudouard (1898) found that the heat of combustion per unit volume of limit mixtures with air for a number of different gases

was approximately a constant, an observation which Burgess & Wheeler (1911), White and others have confirmed, but there are many exceptions and the value for upper and lower limits are dissimilar. There seems to have been little further success in elucidating the problem and in predicting whether a given mixture will propagate flame. In order to develop the conclusions of the previous paper, the influence of the physical properties of the gases comprising the limit mixtures has been further investigated.

In using the determinations of limit mixtures which are to be found in the literature, it is necessary to eliminate those which are not made under comparable conditions, so the guidance they give as to the factors which govern whether flame is propagated or not is rather restricted.

In spite of a considerable number of investigations on the effect of different inert gases on the limit mixtures, it was found necessary to carry out a few additional measurements. Coward & Hartwell (1926) have made a fairly extensive study of the extinction of methane-air flames by carbon dioxide, nitrogen, helium and argon. Measurements have been carried out by others in tubes of rather smaller diameter, wherein the cooling and deactivation at the walls became important factors. Consequently the agreement in the literature between the limits obtained with a given amount of diluent is unsatisfactory and even the relative order of extinguishing power of the various diluents does not agree. Coward & Hartwell (*loc. cit.*), in experiments with methane in 5 cm. tubes, found the order of extinguishing power for nitrogen, carbon dioxide, helium and argon to be $\text{CO}_2 > \text{N}_2 > \text{He} > \text{A}$, whereas Posthumus (1930) found the order $\text{He} > \text{CO}_2 > \text{N}_2 > \text{A}$. Posthumus, however, used 1.6 cm. tubes, and the system studied was $\text{H}_2\text{-N}_2\text{O}$. Booy (1932) found a similar order with methane-air mixtures in 1.7 cm. tubes. Heiningen (1936), however, with H_2 , CH_4 , C_4H_{10} -air systems in 2.2 cm. tubes, arrived at the order $\text{CO}_2 > \text{He} > \text{N}_2 > \text{A}$. All the above workers agree upon the order $\text{CO}_2 > \text{N}_2 > \text{A}$: it is the position of He that varies. Therefore, the effects of CO_2 , He and A upon the limits of inflammability of methane and hydrogen were redetermined. Measurements of the lower limits (l.l.'s) of hydrocarbons have also been made.

2. EXPERIMENTAL

It is useless to compare one propagation limit with another unless the determinations are carried out under similar conditions and unless the diameter of the tube is sufficient to eliminate any differences due to effects at the walls. The influence of convection and flame shape on the results obtained experimentally cannot be eliminated entirely, but for any given combustible the results will be sufficiently comparable under the chosen conditions (except for helium as diluent see p. 201) (cf. Coward & Hartwell 1932).

(a) *Limit mixtures with various diluents*

The same apparatus and procedure as described in part I were employed. The diluent gases were introduced into the tube with their ratio by volume to oxygen

equal to the nitrogen plus argon ratio to oxygen in air. Upward propagation was used as before (except for some experiments with hydrogen mixtures where downward propagation was employed).

The lower limit flames for upward propagation in hydrogen mixtures with argon and helium as diluents were barely visible. They were detected at the top of the tube by a thermocouple of thin copper-constantan connected to a galvanometer. With experience it was possible to correlate the size of flame (as distinct from individual pockets of flame) with the kick of the galvanometer, and to determine the true limit mixture.

The limits found are given in table 1. In the experiments with methane the gases in the flame tube were analyzed after the passage of the flame, using a Bone and Newitt gas analysis apparatus (see table 2).

TABLE 1

atmosphere	l.l.	u.l.
Upward propagation		
hydrogen		
He + 21 % O ₂	7.72	75.7
CO ₂ + 21 % O ₂	5.31	69.8
N ₂ + 21 % O ₂ (air)	4.19	74.6
A + 21 % O ₂	3.17	76.4
limits of error	± 0.03	± 0.3
methane		
CO ₂ + 21 % O ₂	9.0	9.0
N ₂ + 21 % O ₂ (air)	5.26	14.3
He + 21 % O ₂	4.83	16.1
A + 21 % O ₂	4.01	17.3
limits of error	± 0.03	± 0.1
Downward propagation		
hydrogen		
CO ₂ + 21 % O ₂	13.1	—
N ₂ + 21 % O ₂ (air)	9.0	—
He + 21 % O ₂	8.7	—
A + 21 % O ₂	7.0	—
limits of error	± 0.05	—

TABLE 2. GAS ANALYSIS OF COMBUSTION PRODUCTS OF METHANE MIXTURES IN PER CENT. BY VOLUME

diluent	CH ₄	CO ₂	CO	H ₂	O ₂	H ₂ O	inert
l.l.	A	0.4	3.1	0.7	0.2	13.6	74.6
	He	0.3	3.3	0	1.0	12.0	77.6
	N ₂	0.5	4.2	0.2	0	10.5	75.8
	CO ₂	0.4	6.6*	0.5	0.8	3.0	13.7
u.l.	N ₂	1.2	4.2	6.7	7.0	0.9	14.7
	He	2.4	2.7	9.0	9.8	1.6	13.3
	A	2.6	2.5	9.1	12.0	1.4	11.1

* CO₂ as reaction product. † CO₂ as diluent.

For discussion of these results and influence of tube diameter see p. 198. The relative order of extinguishing power of the diluents in upward propagating methane mixtures and downward propagating hydrogen is $\text{CO}_2 > \text{N}_2 > \text{He} > \text{A}$.

For downward propagation, the flames were not hemispherical but flat and rather ragged, tending to set up vibratory effects. Upper limit flames were thin and faster in argon and helium mixtures. The flames with carbon dioxide were similar to those with nitrogen. With methane, those in argon and helium were thinner and rather faster than they were in nitrogen and carbon dioxide.

(b) *Hydrocarbon-air mixtures*

The values recorded in the literature for the limits of propagation of flame in mixtures of the higher hydrocarbons with air are not in good agreement. The proportion of combustible in the l.l. mixture is quite small and the vapour pressure low, rendering measurements open to considerable error. While it has been shown (part I, p. 184) that a graph of the heats of combustion against the reciprocals of the l.l.'s for the lower members of the paraffin series up to butane gives a smooth curve, the values for the higher members as taken from the literature show no such agreement. Careful determinations of the limits for upward propagation at room temperature and atmospheric pressure have therefore been made on a few pure hydrocarbons up to octane (see table 3). The complete curve obtained with these results is shown in figure 1. The vapour pressures of the normal paraffins above octane were insufficient to provide a l.l. mixture at room temperature. Pearson's (1931) adaption of the Rayleigh manometer was used to measure accurately the small pressures involved. Table 4 provides the determinations relating to the purity

TABLE 3

hydrocarbon	l.l.	other values
methane	5.26 ± 0.03	5.24 to 5.45
<i>n</i> -butane	1.93 ± 0.03	1.86
<i>n</i> -pentane	1.62 ± 0.01	1.3 to 1.5
<i>iso</i> -pentane	1.61 ± 0.01	—
<i>n</i> -hexane	1.46 ± 0.01	1.25 to 1.41
<i>n</i> -heptane	1.26 ± 0.01	—
<i>n</i> -octane	1.12 ± 0.01	—
<i>iso</i> -octane	1.15 ± 0.01	—

TABLE 4

substance	boiling point ($^{\circ}\text{C}$)	μ_D^{20}
<i>n</i> -butane	0 to 1.5	—
<i>n</i> -pentane	36.0	1.3577
<i>iso</i> -pentane	28.0	—
<i>n</i> -hexane	67.7 to 68.0	1.3822
<i>n</i> -heptane	98.0 to 98.5	1.3877
<i>n</i> -octane	125.0 to 125.5	1.3975
<i>iso</i> -octane	98.5	1.3915

of the hydrocarbons used. The range of other values from the literature for the l.l.'s (only those determined under similar conditions) are also given in table 3 for comparison. The results are discussed on p. 202.

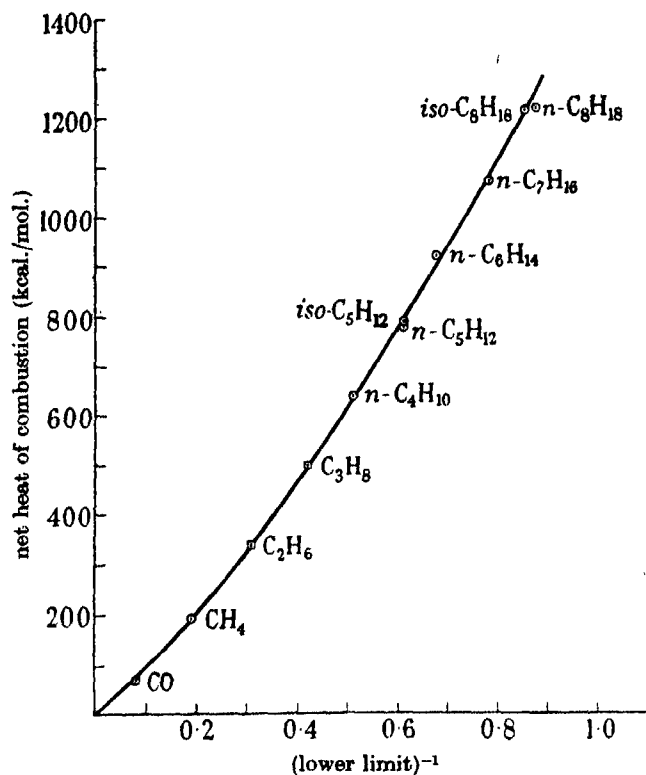


FIGURE 1

3. DISCUSSION

(a) General considerations of flame propagation in limit mixtures

When flame travels through a stationary inflammable gas mixture, or when a similar unburnt mixture flows through a stationary zone of flame, the heat in the flame products is the net heat evolved in the resultant chemical reactions of decomposition and combustion at constant (or nearly constant) pressure of the cold gas, less the heat radiated and conducted away at the walls of the containing vessel or converted to mass movement of the gas, plus heat from any condensation of water on the walls. The flame consists of (1) a region in which the gas mixture, initially cold, is being heated by conduction, (2) a region in which combustion is occurring, and (3) a region in which the products are cooling. The first is assumed to be the region prior to ignition, the combustion being completed at the commencement of stage (3); but some 'slow' combustion without inflammation may occur in stage (1)

and some combustion may continue in the cooling stage (3). A criterion for flame propagation is obviously that $T_m > T'$, where T' is a temperature reached at the commencement of or early in stage (2), such that inflammation must occur once the temperature T' is attained. T_m is the maximum temperature of the flame. It used to be held that the gases are heated by conduction of heat from layer to layer, and at a certain temperature T' the combustion reactions in the heated gas become so fast and self-accelerating that inflammation occurs. This view of flame propagation assumed that the unburnt gas mixture itself generated reaction centres and that ignition occurred when the chain reactions self-accelerated, as in the ordinary passage from slow combustion to ignition. On this basis a theory of flame propagation was suggested by Mallard & Le Chatelier (1883). Applications of this theory have not met with much success. White (1922, 1925) pointed out that the ignition temperature as determined by ordinary methods are generally much lower than the temperatures which he estimated for the flames of limit mixtures, and that the velocity of limit flames cannot be determined from such ignition temperatures.

The experiments described in § 2 show that:

(a) A greater amount of total available heat is required to maintain flame in the l.l. mixtures of higher hydrocarbons than in those of lower hydrocarbons, although the higher members are more readily ignited.

(b) There is no appreciable difference between the combustion of l.l. mixtures of the isomers, whereas their ignition characteristics are different. Both these observations provide further evidence against the inflammability of these limit mixtures being dependent upon the reactions which lead to self-ignition of the mixture.

Lower limit flames have speeds generally less than 20 cm./sec. and the preflame zone at atmospheric pressure is very thin (probably less than 0.05 mm.), so that the heating up and reaction period is only some 0.0005 to 0.0001 sec. Ignition delays are usually much greater than this, for instance, Coward & Hartwell (1926) gave for 6 % methane in 30 % argon-air 0.19 sec. at 950° C, and the shortest ignition delay times were obtained with argon as diluent; the conditions for ignition were, however, different from those which exist in free flames. The delay period for auto-ignition of the unburnt gas ahead of the flame would thus have to be far shorter than experimental work under ordinary ignition conditions would seem to indicate as likely, and the period would have to be little affected by promoters, etc. Further experiments on ignition delays at high temperatures are indeed needed (cf. Lloyd 1946).

The above considerations and the results of the experiments described in part I of this paper indicate that the influence of reactions in the preflame zone is not of major importance, but that the unburnt gas has first to come into contiguity with the flame. The preflame reactions have far less to do with the initiation of the flame in the layer entering the flame zone, than active radicals and molecules with high energy from the flame itself which are met on entering the flame zone. When once the gases encounter a region of high enough temperature containing sufficient concentration of these radicals the combustion is initiated and then proceeds rapidly.

This is not a new conception of flame propagation, for Lewis & von Elbe (1934) developed a theory and applied it to the propagation of flame in ozone, in which they assume that radicals were diffusing into the unburnt from the burning gas (cf. Jost & von Muffling 1938).

The question arises as to whether the maximum flame temperature as suggested by White (1925) and Tanaka & Nagai (1926, 1927) must be the temperature which determines whether the reactions necessary for flame propagation are initiated. Although the maximum flame temperature no doubt is related to the temperature necessary for propagation, with some mixtures the attainment of the maximum flame temperature may take longer than with others and the position will be farther within the inflammation zone. Because of heat loss there will probably be a lower temperature at the forward flame boundary. The attainment of this temperature in the boundary region is the criterion for flame propagation at the limit.

For limit flames, the conditions in the flame front will be discussed with the help of figure 2. T_0 is the initial temperature of the unburnt mixture and the final temperature of the burnt mixture after cooling has taken place behind the flame.

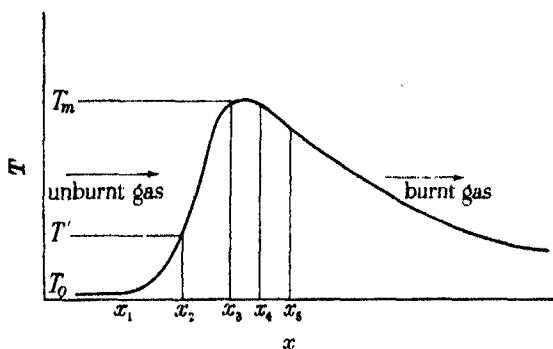


FIGURE 2

T' is a temperature between T_0 and T_m which the unburnt gas has to reach if reaction proceeds and the mixture continues to burn. If this average temperature is not maintained at the flame boundary, flame is not propagated. The temperature at which luminosity commences may be at a slightly higher temperature within the x_2x_3 zone for it will inevitably take a small fraction of time to develop explosive reaction. T' governs the concentration of radicals at the flame boundary.

T_m is the maximum flame temperature given by $h/\bar{C}_p$, where h is the net heat of reaction and $\bar{C}_p$ the mean specific heat of the burnt gas between T_m and T_0 , assuming complete combustion. If T_0 is increased the heat needed to maintain the temperatures T' and T_m is less by the amount supplied (viz.: $\bar{C}_p'(T - T_0)$, where $\bar{C}_p'$ is the mean specific heat of the reactants, assuming $\bar{C}_p'$ varies directly with T), as has been shown by White (1925) to agree closely with experiment. These measurements were not made exactly under the same conditions as accepted in this communication, the

tubes being 2.5 cm. diameter, and so the actual limit mixtures and flame temperatures are slightly different, but using the more recent calorific values and specific heats (see table 5) the conclusion drawn by White is definite. Agreement is not so close with hydrogen probably because of the effect of tube diameter and convection.

TABLE 5

mixture with air	calorific values of limit mixtures		$h_1 - h_2$	$\bar{C}_p(400^\circ - 17^\circ)$	$100 \frac{h_1 - h_2 - h_3}{h_1}$
	at 17° h_1	at 400° h_2			
H ₂	543.5	364.0	179.5	272.5	-17
CO	110.3	770.5	332.5	273	5.5
CH ₄	1202	917	285	282	0
C ₂ H ₄	1088	789	299	283	0

At the limits the rise in temperature ($T_m - T'$) will be comparatively small, the available heat having been used mainly in heating the gas mixture from T_0 to T' .

The position x_2 where the unburnt gas reaches T' will be dependent on T_m and on the gradient between x_2 and x_3 ; the latter will be dependent on the heat loss and on the reaction rate. The value of T' for a given combustible will depend on the nature of the reaction and the diffusion of radicals at T' , though the physical properties of the mixture, specific heat and conductivity, may so affect the energy distribution that T' will appear to be altered. At the limit, any small reduction in composition which lowers T_m , or any change causing a small increase in heat loss reduces the temperature gradient between x_3 and x_2 to zero and T' is no longer maintained; change of conductivity will affect the heat loss from the flame.

The temperature T_m as given by $h/\bar{C}_p$ is not necessarily attained because of loss of heat from the system by radiation; furthermore, as already stated, reaction may not be completed and the composition of the products may not be fixed until zone 5 has been reached. Nevertheless, there will be a position, or zone x_2 to x_4 , in which T will be a maximum for a limit mixture and it will bear close relation to $h/\bar{C}_p$.

The energy converted from chemical to thermal energy in the flame is h_0 , since any small element of the unburnt mixture entering the flame must possess energy $h_0 + \int_{T_0}^{T'} C_p dT$, there is locally an excess of energy, but such excess is compensated by an equivalent amount of energy $\int_{T_0}^{T'} C_p dT$ having to flow from the flame into the incoming gas in order to heat it to T' . The process of distribution of the energy within the zone x_2 to x_4 will depend on the rate of reaction and the diffusivity of the products as pointed out by Lewis & von Elbe (1934). Much has to be learnt about the structure of the flame front; T' even if it can be considered as an average condition of the unburnt gas at the flame boundary cannot be readily estimated. For the consideration of the behaviour of limit mixtures, particularly lower limit mixtures in which the reaction is probably complete in quite a narrow region x_2 to x_3 , the question whether T_m is a sufficient criterion for flame propagation will be

examined, bearing in mind that the average value of T' will be a somewhat lower temperature. The difference between T_m and T' will be at a minimum in limit mixtures. For an estimate of T' a knowledge of the maximum temperature, the temperature gradient and the heat loss would be needed, or direct spectroscopic determination of the temperatures throughout the flame zone and boundary region.

This view does not preclude that with some mixtures, reaction occurs in the pre-flame zone and renders inflammation more rapid, or even that a dual process exists; but the experimental evidence indicates that the building up of reaction centres in the preflame zone of the unburnt gas is not usually important in the short time available. Nevertheless, as White (1922), Prettre (1931) and others found, many substances can give rise to cool flames at quite low temperatures in certain ranges of pressure and Townend & Hsieh (1939) have shown that under certain conditions with certain mixtures, cool flame propagation accompanies ordinary flame propagation. With cool flames, the process of flame propagation is more closely related to ordinary ignition processes, and the criterion for propagation may then be different.

(b) *Discussion of experimental results for l.l. mixtures with various diluents*

These considerations can now be applied to the experimental data in § 2.

The flame temperatures T_m are given in column 7 of table 6 for all the mixtures investigated.

TABLE 6

1	2	3	4	5	6	7	8
mixture	l.l.	H	h	$\bar{C}_p$	K	T_m (°C)	T_m (uncorr.) (°C)
	(downward)						
H ₂ -O ₂ -CO ₂	13.1	8.95	7.57	9.93	231	780	—
H ₂ -O ₂ -N ₂	9.0	6.15	5.21	7.19	202	743	—
H ₂ -O ₂ -He	8.7	5.94	5.03	5.56	562	923	—
H ₂ -O ₂ -A	7.0	4.78	4.05	5.50	163	754	—
	(upward)						
CH ₄ -O ₂ -CO ₂	9.0	19.18	15.31	11.94	167	1301	1450
CH ₄ -O ₂ -N ₂	5.26	11.21	8.96	8.11	156	1123	1250
CH ₄ -O ₂ -He	4.83	10.29	7.83	5.96	532	1329	1515
CH ₄ -O ₂ -A	4.01	8.66	6.39	6.01	127	1081	1280

Column 1. Mixture: combustible with diluent and oxygen in same proportion as N₂ (+ A):O₂ in air.

Column 2. Percentage of combustible in the l.l. mixture.

Column 3. Gross heat of combustion in kcal./mol.

Column 4. Net heat of combustion (corrected) kcal./mol.

Column 5. Mean molecular heat of products (corrected) to T_m .

Column 6. Conductivity of mixture at 600° C in kcal./cm.² sec. cm. °C. $\times 10^6$.

Column 7. Maximum temperature $T_m = T_0 + h/\bar{C}_p$, $T_0 = 18^\circ$ C.

Column 8. Maximum temperature (uncorrected for incomplete combustion).

Although the composition of the cold burnt gases does not provide precise information for the estimation of T_m , the figures in columns 4 and 5 for methane combustion, have been corrected to allow for the results of the analyses given in table 2, which indicate that the methane is not quite completely burnt. For the downward propagating hydrogen mixtures, the combustion is known to be nearly complete and no correction has been made. No doubt, for methane mixtures, some of the gas escapes combustion in the space between the flame boundary and the walls; it has not been attempted to make separate allowance for this, but the allowance is included in the overall correction.

Figures are inserted in column 6 to indicate approximate values for the conductivity of the unburnt gases; where experimental values are not available at high temperatures, the Sunderland formula for the temperature coefficient has been assumed. The influence of conductivity is quite definite for the helium mixtures, but the differences in thermal conductivity are not sufficient to account entirely for differences in T_m for the other mixtures (cf. Coward & Hartwell (1926)).

In connexion with the neglect of heat losses, during the experiments on the upward propagation of hydrogen l.l. and u.l. flames some experiments were made to test to what extent a change in the heat received by radiation to the walls affected the results. The walls were blackened in one set of experiments and silvered in the other; there was very little difference in the results.

hydrogen (upward propagation)	l.l.	u.l.
normal (glass)	4.19	74.6
blackened	4.12	74.3
silvered	4.17	74.8

Leaving aside discussion of the results for helium mixtures, in table 6 the indication is that the maximum temperatures are not very different for any l.l. mixture of a given combustible. The value obtained for the CO_2 mixture with methane is high; but the mixture is just at the bend of the l.l. and u.l. curve (see figure 3 and p. 201). The results agree quite satisfactorily with the values (see table 7) calculated from the measurements of Coward & Jones (1938) using mixtures of methane and air with the same diluents. The helium mixture is exceptional as before and the 33 % nitrogen mixture is also rather close to the bend of the curve.

The value for the l.l. methane-air mixture is the same as the value obtained by the authors and if similar allowances had been made for unburnt combustible no doubt the other values would also agree.

The results obtained for upward propagation in hydrogen mixtures, in which the combustion is incomplete are so influenced by preferential diffusion of hydrogen into pockets of flame that they do not serve for comparison; they are given in table 8 because they show that the effect of helium as diluent is to counteract by dissipation of heat the diffusion of the hydrogen into combustion centres. The limits for downward and upward propagation in helium mixtures are far closer than for argon mixtures. (A nominal temperature, 600°C , is used for estimation of $\bar{C}_p$ and K .)

The measurements of the l.l. mixtures of hydrogen and of deuterium with air or with 20 % O_2 and 80 % helium, neon or argon by Clusius & Gutschmidt (1936) show that in helium mixtures the effect of convection is least, but the dissipation of energy

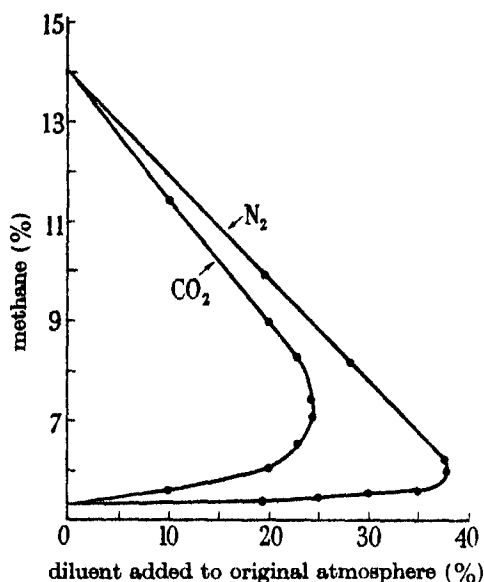


FIGURE 3

TABLE 7

mixture	l.l.	h	$\bar{C}_p$	T_m (°C)
19 % CO_2 + air + methane	6.0	11.47	9.06	1282
19 % N_2 + air + methane	5.4	10.31	8.14	1282
19 % He + air + methane	5.3	10.13	7.66	1338
19 % A + air + methane	4.85	9.26	7.56	1241
33 % A + air + methane	4.57	8.74	7.14	1241
33 % N_2 + air + methane	5.65	10.80	8.19	1338

TABLE 8. UPWARD PROPAGATION

mixture	l.l.	h (uncorrected)	K (for reactants at 600° C)	$h/\bar{C}_p$ ($\bar{C}_p$ for reactants to 600° C)
H_2-CO_2	5.31	3.08	178	300
H_2-N_2	4.19	2.42	170	330
H_2-He	7.72	4.47	559	790
H_2-A	3.17	1.83	132	330

from the flame front greatest. In argon mixtures, on the other hand, the convection effect is greatest giving a wide difference between downward and upward propagating mixtures, but the dissipation is least and therefore the lowest percentage of hydrogen or deuterium is required for a l.l. mixture.

The flame temperatures of the helium mixtures are high in comparison with those for other diluents; this is presumably due to the high conductivity of the helium which dissipates the energy from the flame front and increases the proportion of heat lost. In agreement with this, the authors have found that the lower limit of methane with helium diluent is decreased from 4.83 to 4.5 when the tube diameter is increased from 5 to 10 cm., showing that with helium mixtures in 5 cm. tubes the effect of the loss of heat to the walls is not yet negligible, as is nearly so with the other diluents. With argon as the diluent, the l.l. was unaltered by increasing the diameter of the tube from 5 to 10 cm.

The conductivity factor explains the different relative extinguishing power of helium in tubes of different diameter which was pointed out in the introduction. In tubes of diameter less than 1.7 cm., helium has a greater extinguishing effect than carbon dioxide, nitrogen or argon but as the diameter increases its relative effect becomes progressively smaller. In 2.2 cm. tubes it is less efficient than carbon dioxide but is still better than nitrogen and argon; when the tube diameter reaches 5 cm., it is superior only to argon.

The curves obtained by Coward & Hartwell (1926) for the extinction of flame by the addition of nitrogen or carbon dioxide to mixtures of methane and air are given in figure 3. The values of T_m along the lower limit boundary are as follows:

TABLE 9

N ₂ % added to the air	CH ₄ (%)	<i>h</i>	$\bar{C}_p$	T_m (° C)	CO ₂ % added to the air	CH ₄ (%)	<i>h</i>	$\bar{C}_p$	T_m (° C)
0	5.3	10.12	8.10	1260	0	5.3	10.12	8.10	1260
10	5.4	10.31	8.11	1290	5	5.44	10.40	8.34	1260
20	5.5	10.50	8.12	1310	10	5.61	10.72	8.56	1270
30	5.6	10.70	8.15	1330	15	5.8	11.08	8.79	1280
					20	6.07	11.59	9.04	1300
					23	6.57	12.54	9.28	1370

No correction has been made for incomplete combustion as no analyses of end products were made.

The upward trend with increase in diluent is probably due to increasing incompleteness of the combustion in the flame boundary; for the addition of 20 % of the two diluents, the temperatures are almost the same, but in the neighbourhood of the bend of the curve the maximum temperature becomes considerably higher (see above). Similarly with l.l. carbon monoxide mixtures diluted with nitrogen or CO₂, the temperature remains fairly constant at about 1180° C rising towards the bend of the curve. For ethane-air mixtures (Jones & Kennedy 1932), and butane-air mixtures (Jones & Kennedy 1933), diluted with nitrogen and CO₂, some figures are given in table 10.

For butane, the intermediate values can be interpolated in accordance with the amount of diluent added. The accuracy of these measurements is insufficient to establish whether the increase of T_m is real; where there is an apparent increase, it

is likely to be due to incomplete combustion in the flame front. The apparent increase is greater with carbon dioxide as diluent; CO_2 and H_2O being products, addition of either of these gases would decrease the amounts produced in reaction and raise the apparent value of T_m , unless allowance is made. The same cause may account for the rather high value for T_m (about 1350°C) from the limit values for methane mixtures diluted with water (Coward & Gleadall 1930).

Though far from complete, the experimental evidence indicates that the maximum temperature, and therefore the boundary temperature, for l.l. mixtures of a given combustible tends to be constant, apart from minor influences.

TABLE 10

N_2 % added to the air	ethane (%)	H	$\bar{C}_p$	T_m ($^\circ\text{C}$)	CO_2 % added to the air	ethane (%)	h	$\bar{C}_p$	T_m ($^\circ\text{C}$)
0	3.1	10.25	8.26	1260	0	—	—	—	1260
10	3.1	10.25	8.26	1260	10	3.32	11.33	8.76	1310
20	3.1	10.25	8.25	1260	20	3.58	12.21	9.18	1350
30	3.1	10.25	8.23	1260	30	4.03	13.76	9.88	1400
	butane (%)					butane (%)			
0	1.86	11.82	8.52	1410	0	—	—	—	1410
35	2.1	13.10	8.61	1540	20	2.2	13.98	9.61	1470

(c) *Discussion of limits for propagation in hydrocarbon mixtures*

Burgess & Wheeler (1911) found that the relationship $LC = k$ (where L is the percentage of combustible in the l.l. mixture, C is the net heat of combustion of the fuel and k , constant = 1059) held for the paraffins up to pentane. However, the values for the limits were not the same as those generally accepted to-day; they were determined in a glass sphere with central spark ignition and therefore under different conditions. The results of the new measurements given on p. 193 show, on the contrary, that the value of k increases as the paraffin series is ascended and there is therefore an increase in T_m , for $\bar{C}_p$ shows only a relatively small change. The values increase asymptotically to about 1600°C where the effect of dissociation only begins to become appreciable. The increasing values of T_m indicate that the higher hydrocarbons are progressively more difficult to inflame than the lower, for the mixture has to be richer for flame propagation to occur.

Since the ignition temperatures of the n -paraffins decrease with increase of the chain length, the conditions for flame propagation do not seem to depend upon the stability or on the ignition characteristics of the compounds but, as indicated in the earlier discussion, inflammation occurs when the number of reaction centres derived from the flame are sufficient to inflame the unburnt mixture. Table 11 compares the values of T_m for those hydrocarbons the limits of which have been determined with their ignition temperatures at 1 atmosphere as measured by Townend & McCormac (1939).

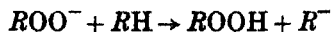
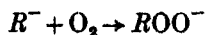
It is quite probable that the minimum flame boundary temperature T' for the inflammation of all the hydrocarbons has about the same value but a slightly higher concentration of the larger hydrocarbon molecules are needed to maintain the reaction rate in the flame front and therefore T_m and T' appear to be higher. The temperature distribution in the flame no doubt changes with the complexity of the hydrocarbon as is indicated by the character of the flames. Apart from the decrease in concentration and its effect on the reaction velocity as the complexity increases, molecules of the higher hydrocarbons presumably take longer to be broken down and therefore the energy released is not shared so quickly with neighbouring molecules. There is indication of this in the characteristics of upper limit flames; some of the hydrocarbon molecules penetrate behind the flame boundary before being burnt and so the boundary becomes less pronounced.

TABLE 11

hydrocarbon	l.l.	T_m (° C)	ignition temperature (° C)
methane	5.26	1255	650
n-butane	1.93	1445	480
n-pentane	1.62	1485	470
iso-pentane	1.61	1481	—
n-hexane	1.46	1568	275
n-heptane	1.26	1669	255
n-octane	1.12	1675	245
iso-octane*	1.15	1606	530

* 2, 2, 4-tri-methyl pentane.

The oxidation of the hydrocarbons (RH) is a complicated process and the mechanism has not been fully unravelled, but the experimental facts seem to indicate that it is governed by the reactions:



spontaneously breaking to simple products CH_2O , CO and OH ,
 CH at higher temperature

stabilizing under certain conditions, or providing OR or OH in others

A flame, since it provides OH , CH and C_2 radicals, etc., is able to initiate inflammation if there are sufficient of such radicals to bring about reaction in a certain minimum number of molecules entering the flame boundary, by such reactions as $OH + RH \rightarrow H_2O + R^\cdot$. When inflammation is thus occasioned there is a rapid release of energy, the temperature of the flame boundary which is losing heat to the unburnt gas being thereby maintained.

The values of the l.l.'s for the olefines lie slightly below the curve for the saturated hydrocarbons; the point for toluene lies on the curve but that of benzene is much

lower. Acetylene also gives a lower value. It is quite possible that there is some slight preflame dissociation with the unsaturated hydrocarbons which lowers the flame boundary temperature, as is indicated by C—C bands and the appearance of carbon, and also by large departures from the Le Chatelier mixture rule for mixtures of acetylene and hydrogen or hydrocarbons. The values for most other carbon compounds lie about the curve for the hydrocarbons, but other combustible substances which readily give rise to cool flame phenomena may have quite different values for T_m at the limits, for instance, hydrogen sulphide seems to give a value of about 705° C and carbon disulphide 420° C.

Le Chatelier's Rule, that mixtures of limit mixtures are limit mixtures, is a useful approximation and implies that the several combustibles do not influence each other's behaviour in a limit mixture. It holds well for combustibles of the same character (e.g. hydrocarbon vapours) and even for gases with such different physical properties as hydrogen and methane (in downward propagating mixtures). For mixtures which contain combustibles readily exhibiting preflame or cool flame combustion, e.g. H_2S , CS_2 , etc., the law does not hold, cf. White (1925).

(d) *Relation between upper and lower limits*

Another test of the conclusion that a temperature T' , depending on the specific heat and heat of reaction, is the criterion for flame propagation can be made. In the u.l. mixtures there is excess of combustible, the latter itself acting as diluent, so if no factor is influencing the limit other than h_p and $\bar{C}_p$ and the excess combustible remains largely unchanged after the passage of flame, it should be possible to estimate the value of the u.l. in oxygen by allowing for the change in the molecular heat of the mixture due to the substitution of nitrogen by the combustible vapour. If x , y and z are the percentages of fuel, oxygen and nitrogen respectively and $\bar{C}_{p(x)}$ and $\bar{C}_{p(z)}$ are the molecular heats of nitrogen and fuel from 18° C to T_m (assuming T_m to be the same for the u.l. mixture as for the l.l.) then:

$$\text{u.l. (O}_2\text{)} = \frac{\left[x + z \frac{\bar{C}_{p(z)}}{\bar{C}_{p(x)}} \right] 100}{x + z \frac{\bar{C}_{p(z)}}{\bar{C}_{p(x)}} + y}$$

TABLE 12

	u.l. (air)	u.l. (O ₂)	
		calc.	obs.
H ₂	74.6	94.8	94
CO	74.0	94.5	94
NH ₃	27.0	79.9	79
CH ₄	14.3	73.5	60

At the u.l. for hydrocarbons, combustion to CO₂ is not complete and, without a knowledge of the extent of combustion in the flame front and correction, the method cannot give values in agreement with observed values, but where com-

bustion is complete in the flame, the u.l. values estimated from the l.l.'s agree quite well. The relationship between the two limits can be seen by reference to the values obtained by Jones (1929) for CO mixtures diluted with nitrogen and carbon dioxide (table 13). Within the error of the experiments the values of T_m are fairly constant, though with a tendency for lower values of T_m for the u.l.'s. The higher values for T_m at the l.l.'s are partly due to the rather high value (13.3) for the l.l. mixture: the l.l. for CO is usually given as 12.5 which would make $T_m = 1110^\circ \text{C}$. Complete combustion has been assumed. The position of the bend of the curve plotting the inflammability limits (see figure 3) is slightly on the rich side of the stoichiometric mixture; excess of oxygen would be unfavourable to this reaction. For hydrocarbon vapours higher than methane a similar tendency is shown, the displacement being greater the higher the hydrocarbon in the series. This is presumably due to the increase in the molecular proportion of oxygen to hydrocarbon required for complete combustion which has the effect of decreasing encounters between the two molecules. A richer mixture is therefore favourable to reaction because although the extent of oxidation decreases with increasing richness of mixture the number of collisions between fuel and oxygen molecules increases. A higher proportion of incompletely burnt fuel remains in the products and an apparently higher value of T_m is obtained.

TABLE 13

			T_m					T_m
CO	O ₂	N ₂	(° C)	CO	O ₂	N ₂	CO ₂	(° C)
72.0	5.9	22.1	1020	72.0	5.9	22.1	0	1020
45.4	5.6	49.0	1020	47.9	6.5	24.8	20.8	1050
29.5	5.7	64.8	1030	39.0	6.8	25.8	28.4	1050
24.8	5.7	69.5	1030	27.3	7.2	27.3	38.2	1060
20.3	5.7	74.0	1030	21.8	7.8	29.5	40.9	1128
16.8	5.6	77.6	1020	18.6	8.6	32.5	40.3	1230
14.3	5.9	79.8	1070	16.5	10.3	39.2	34.0	1220
13.9	6.0	80.1	1080	15.5	12.0	45.4	27.3	1180
13.7	9.8	76.5	1230	15.0	13.2	49.8	22.0	(1220)
13.4	13.2	73.4	1190	14.3	14.4	55.1	16.2	1160
13.3	18.1	68.6	1180	14.0	16.6	62.7	6.7	1190

(e) *Discussion of experimental results for upper limit mixtures with various diluents*

The values for the u.l. for upward propagation of the mixtures investigated are given in table 14. The u.l.'s for upward propagation in hydrogen mixtures are very closely the same as for downward.

The products of combustion of the methane mixtures were analyzed after the flame had travelled through the tube; the results were given in table 2. With hydrogen at the upper limit, the combustion of the oxygen to water is complete.

The values of T_m for hydrogen are in approximate agreement with the values obtained from the measurements by Jones (1929) for a range of limit mixtures in which hydrogen:nitrogen proportion is changed (table 15). The measurements were made in 5 cm. tubes with upward propagation (above 11 % the flame front is

normal and little influenced by convection). The value of the u.l. mixture in air was slightly lower than that given in table 14 which makes T_m rather greater.

TABLE 14

1 mixture	2 u.l.	3 H	4 h	5 $\bar{C}_p$	6 K	7 T_m ($^{\circ}\text{C}$)
$\text{H}_2\text{-O}_2\text{-CO}_2$	69.8	8.67	7.35	8.02	609	934
$\text{H}_2\text{-O}_2\text{-N}_2$	74.6	7.29	6.18	7.00	642	902
$\text{H}_2\text{-O}_2\text{-He}$	75.7	6.96	5.90	6.52	745	909
$\text{H}_2\text{-O}_2\text{-A}$	76.4	6.78	5.75	6.53	647	898
$\text{CH}_4\text{-O}_2\text{-CO}_2$	9.0	19.18	15.31	11.93	167	1301
$\text{CH}_4\text{-O}_2\text{-N}_2$	14.3	19.28	14.40	8.60	180	1581
$\text{CH}_4\text{-O}_2\text{-He}$	16.1	18.75	11.93	7.41	518	1628
$\text{CH}_4\text{-O}_2\text{-A}$	17.3	18.50	10.94	7.60	165	1458
$\text{H}_2\text{-N}_2\text{O-N}_2$ (a)	29.0	13.11	11.53	8.01	333	1458
$\text{H}_2\text{-N}_2\text{O-N}_2$ (b)	65.8	12.64	11.12	7.84	581	1438

Column 1. Mixture: combustible with diluent and oxygen in same proportion as $(\text{N}_2 + \text{A}) : \text{O}_2$ in air.

Column 2. Percentage of combustible in u.l. mixture.

Column 3. Gross heat of combustion of the limit mixture in kcal./mol. (for complete combustion to CO_2 and water).

Column 4. Net heat of combustion (corrected for analysis) in kcal./mol.

Column 5. Mean molecular heat of products between 18°C and T_m .

Column 6. Conductivity of reacting mixture at 600°C in kcal./cm.² sec. $^{\circ}\text{C} \times 10^6$.

Column 7. Maximum temperature (uncorrected for heat loss) $T_m = T_0 + h/\bar{C}_p$.

TABLE 15

limit mixture			K	T_m ($^{\circ}\text{C}$)
H_2	O_2	N_2		
72.0	5.0	22.1	620	970
51.6	5.6	42.8	480	930
29.6	5.3	65.1	340	870
15.2	5.1	79.7	240	850
11.5	5.1	83.4	220	850

The trend in these figures is no doubt due to the effect of increasing conductivity as the proportion of H_2 increases.

The values of T_m for the u.l. for hydrogen (upward propagation) lie close to the value obtained for the l.l. for both downward and upward propagation with helium as diluent; the conductivities of the mixtures are comparable and the temperatures of the flame front controlling propagation have much the same value in each case. One reason for the lower values of T_m for the l.l.'s is to be found in the lower heat loss with these mixtures, which have a much lower conductivity than helium diluted mixtures or u.l. mixtures with excess of hydrogen.

The bend of the curve expressing the inflammability limits for hydrogen mixtures is also in an exceptional position on the weak side of the position for the stoichiometric mixture. This is probably due to the high diffusivity of hydrogen causing

heat to be removed from the flame front, thus a smaller proportion of hydrogen favours reaction.

The values of T_m in table 14 for mixtures of N_2O , hydrogen and nitrogen at the u.l. are interesting because, as with other mixtures in which combustion is continued well behind the flame front, the estimated values are high. From the character of these flames with nitrous oxide it is quite obvious that oxidation is slower than with mixtures containing oxygen; the flames themselves are slower and the products luminous for some distance behind the flame front. The reaction in the flame front cannot be well represented by $N_2O + H_2 = N_2 + H_2O$ as assumed and the flame temperature is probably considerably lower than is estimated.

The values of T_m in table 14 obtained for the u.l. methane mixtures are higher than those for the l.l. mixtures (except for the CO_2 mixture where T_m is the same for both, the point being on the bend of the limit curve). This is probably due to slower reactions and to incomplete combustion in the flame front. Although corrected, using the results of the analyses of the products, the actual values do not mean much; the temperature cannot be determined without knowledge of the initial reactions in the flame front, and even so in the first encounter of unburnt gas with the flame boundary, the time for reaction may be short compared with the time for temperature equilibrium to be established and the local temperature can be far higher than the average.

The flames of the u.l. methane mixtures have a rather different structure from those at the l.l.: the flame is shaped more like a paraboloid and has a faint, short conical tail, whereas the l.l. flame is nearly hemispherical with a rather ragged lower edge and no tail. This appearance indicates that reactions continue to take place after the first region of contact of the unreacted gases with the flame. These characteristics are still more noticeable in the flames of higher hydrocarbons. The products of reaction at the flame front are both CO_2 and CO , resulting from reactions such as $CH_4 + O_2 \rightarrow (CH_3O_2^-) \rightarrow (CO + H_2 + CO_2 + H_2O)$. If the reaction produced CO_2 from $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, then with the N_2 mixture, T_m should be about $1850^\circ C$, whereas for $CH_4 + O_2 \rightarrow CO + H_2 + H_2O$, T_m would be about $1080^\circ C$. The real value probably lies nearer the latter figure. Reactions which are continued behind the flame front give rise to high values of T_m . At the u.l., where there is a considerable deficiency of oxygen, any molecule of the combustible which is not consumed at the flame front may travel some distance before it reaches its final degree of oxidation, hence the difference between the structure and temperature gradient of upper and lower limit flames.

This difference is also indicated by the behaviour of inhibitors like methyl iodide or bromide, which influence particularly the u.l.'s. These substances considerably increase the total thickness of the flame and raise the heat loss to the walls by slowing down the reaction in the flame and decreasing the number of active radicals available in the flame front to start inflammation. The calculated values of T_m would consequently be very high. The value of T' would no doubt be somewhat higher than it is for an uninhibited mixture, because propagation is not only

dependent on the temperature and therefore on the average energy of the molecules in the flame front, but also on the radicals in the flame front suitable for initiation of the reactions in the unburnt gas. If the necessary radicals are reduced in number by an inhibitor a higher temperature is needed to induce flame propagation.

It is curious that the character of the flames of limit mixtures of hydrocarbons in the presence of 'promoters' is often considerably changed without alteration of the limit. This is because for the small quantity of 'promoter' added, the inflammation temperature of the combustible is little changed: the effect of the 'promoter' only comes later in the body of the flame after the first stages of reaction. In one case however, ethyl nitrate, a definite effect on the upper limit of the combustion of butane was observed. If the change of the reaction rate within the flame due to the additive is sufficient, it will have its effect on the boundary temperature. Such experiments as have been made indicate that inhibitors such as lead tetraethyl, tin tetramethyl, selenium diethyl (Tanaka & Nagai 1927) and iron carbonyl (Thompson 1932) have only a small effect on l.l.'s, but very definitely narrow the upper limit, as would be consistent with the conclusion that their inhibitory action is exerted on the reactions within the flame boundary. Dufraisse & Le Bras (1936) ascribed the extinctive effect of carbon tetrachloride to be due partly to hindrance of the oxidation of the combustible owing to its physical properties and partly to the inhibition of the chemical process of oxidation. The diffusion of radicals into the unburnt gas being an important feature of the process of flame propagation, the presence of large molecules with slow average velocity will tend to raise T' , the presence of such substances as carbon tetrachloride, and even carbon dioxide, will produce such a tendency. The fact that the values for T_m are low for mixtures containing hydrogen can in the opposite way be ascribed to the easier diffusion of radicals.

It is not possible without further knowledge of the initial reaction in the flame front to estimate the true values for T_m much less for T' , for u.l. mixtures of hydrocarbons and other organic compounds with air, but as already pointed out when the reaction in the flame front is simple it can be shown that there is little difference between the value for the u.l.'s and l.l.'s.

4. CONCLUSION

A review of the effects of various diluents on the upper and lower limit mixtures for the propagation of flame with various combustibles has led to the conclusion that, whether combustion takes place or not is dependent upon the temperature of the flame being sufficient to maintain a certain boundary flame temperature which provides a certain concentration of active radicals in the boundary region; inflammation is produced in the unburnt gas mainly from the radicals derived from the flame. This does not preclude the possibility that in some cases a double process may be occurring, as indicated by Townend's researches, the one due to cool flame reactions in the unburnt gas and the other due to the above process of inflammation: but for limit mixtures this is exceptional. It should also not be assumed that,

because for mixtures near the limits little reaction takes place in the unburnt gas before entering the flame, this is necessarily so for fast burning mixtures.

It is shown to be possible on this view to estimate approximately whether a given mixture of combustibles and diluents should propagate flame or not, provided the specific heats are known. This, however, is not possible for u.l. mixtures of hydrocarbons and organic substances without more knowledge of the reactions in the flame front.

Flame structures, particularly those at low pressures, are being investigated by spectroscopic methods in this laboratory. Experiments have also been made with promoters on the velocity of flames and the bearing of the above conclusions on the mechanism of flame propagation is being further studied. Preliminary results with butane-air mixtures have shown that the presence of ethyl nitrate, diethyl peroxide and nitrogen peroxide has little influence on the flame speed. The additives, particularly nitrogen peroxide, appear to retard rather than increase the rate of propagation.

The authors are grateful for discussion with Mr P. Lloyd, to the Gas Light and Coke Co. for their grant of the Fellowship which enabled this work to be carried out and also to Messrs Rolls Royce Ltd., for further assistance at a later stage.

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BAKERIAN LECTURE

Some problems in connexion with the development of a high speed Diesel engine

BY H. R. RICARDO, F.R.S.*

(Delivered 6 November 1947—Received 12 November 1947)

[PLATE 4]

When invited to deliver the Bakerian Lecture, I felt very diffident about accepting, for I am a mechanic rather than a scientist, and the tale I am going to tell is mostly one of mere plumbing and ironmongery. I have chosen, as a theme, my own personal experiences over the development of high speed Diesel engines, but I would like to emphasize, at the outset, that this was no single-handed effort for, not only had I the enthusiastic support of my small but very capable staff, but also the most unstinted help and advice from the technical staffs of manufacturing firms, from such establishments as the Royal Aircraft Establishment and The National Physical Laboratory, combined with financial help and encouragement from the Air Ministry and the Shell Company; so that nobody could have had happier or more favourable circumstances than I.

I think perhaps I should try and explain, as briefly as possible, the circumstances.

We established our experimental laboratory at Shoreham during the closing phases of the 1914 War, our intention being to carry out research and development work on internal combustion engines, with a view to providing manufacturers with advice and up-to-date designs.

Our first large scale undertaking was a research on volatile fuels for spark ignition engines carried out on behalf of the Shell Company and, in parallel, a research into the possibilities of the sleeve valve engine for aircraft under a research contract for the Air Ministry.

The research on volatile liquid fuels revealed, among other interesting matters, that the tendency of any fuel to detonate was the dominating factor controlling the performance of spark ignition engines—this tendency we now define as the octane number of the fuel—and also that such engines could not be expected to operate satisfactorily on a fuel the final boiling point of which exceeded about 180° C.

At that date, the heavy demand for petrol of low boiling point had left the oil companies with an embarrassingly large proportion of heavier distillates, which were becoming a drug in the market.

The Diesel engine had, of course, long since been evolved to digest these heavier fractions, but it had been developed only in the very heavy and low-speed form and

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was, therefore, suitable only for stationary or marine use, but by far the largest consumer of fuel was road transport, which was limited to the use of petrol. It became apparent, therefore, that there would soon be a crying need for a light high speed Diesel engine with an all-round performance comparable with that of the petrol engine. Again the Air Ministry were anxious to explore the possibilities of a Diesel engine for aircraft.

And now, perhaps, I had better attempt to define what I mean by the term 'high-speed engine'. High speed and low speed are, of course, relative terms and there is no obvious dividing line; clearly a high speed engine can run slowly, and why should not a low speed engine be made to run fast? The dividing line is to be found in an entirely different conception of design. In the low speed engine, the dynamic forces set up by the inertia of the pistons and other moving parts are relatively small, hence these parts can be made very massive, but dynamic forces increase as the square of the speed and, in a high speed engine, they become the dominating factor. The essence, therefore, of high speed engine design is the use of as rigid a structure as possible containing the lightest possible moving parts, while stiffness rather than strength becomes the goal to aim at.

We realized fully that to compete successfully with the petrol engine on the road or in the air, we should have to aim at the development of a Diesel engine which could run nearly, if not quite, as fast, would be equally as versatile and flexible and, if at all possible, equally simple and economical to maintain. Inevitably the Diesel engine would be more expensive to produce but this, we hoped, would be offset by its lower fuel consumption.

In the case of the spark ignition engine, control of power is effected solely by varying the quantity, not the quality, of externally carburetted air, hence only the pressure scale is varied and the thermal cycle, apart from direct heat losses and other secondary factors, is unaffected by variations of power. In that of the Diesel engine, the power is varied by cutting off the supply of fuel earlier or later in the expansion stroke, thus the smaller the quantity of fuel admitted per cycle, the larger the effective expansion ratio and the higher the thermal efficiency. Again, as the fuel quantity is reduced, so the mean temperature falls and with it both the direct heat losses and those due to change of specific heat and dissociation.

In the Diesel cycle, therefore, the thermal efficiency increases progressively as the power is reduced; this is a very important consideration as applied to road transport where the average operating load is only 30 to 40 %.

As I have always visualized it, the process of combustion in a petrol engine cylinder is somewhat as follows: The spark passes, leaving behind it a thin thread of flame; this minute nucleus builds up, slowly at first, somewhat after the manner of a soap bubble and, if left undisturbed, would spread thus throughout the whole of the combustion chamber, a relatively slow process. It is not left undisturbed, for the bulk of the mixture is in a high degree of turbulence so that the flame front is torn to shreds which are distributed rapidly throughout the whole combustion space, as it were by handing round the fiery torch, and the rate at which general

inflammation then takes place, is controlled almost solely by the intensity of turbulence. There will thus be first a delay period during the building up of the initial nucleus which will be more or less constant in time, followed by a pressure rise due to the spread of flame more or less constant in terms of crank angle, see figure 1, which shows two typical indicator diagrams taken from a petrol engine cylinder.

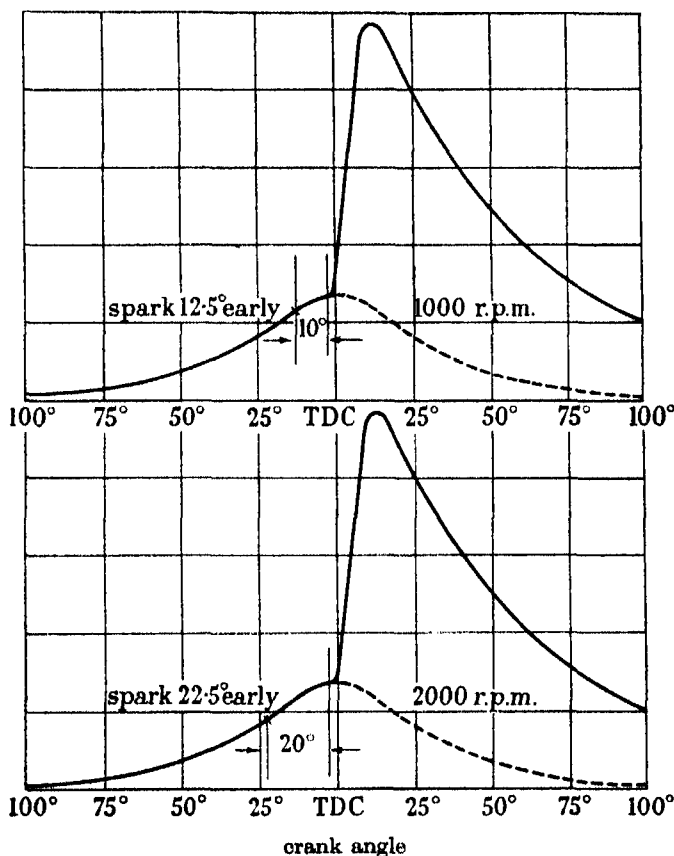


FIGURE 1. Diagrams showing increase of 'delay' period with increase of speed.

In the Diesel engine, the process of combustion is necessarily somewhat different. In this case, air alone is compressed in the cylinder to a pressure and temperature well above the self ignition temperature of the fuel. Into this highly heated air, the fuel is injected as a finely divided liquid spray. As we visualized it, each minute droplet would be very quickly surrounded by an envelope of its own vapour which, in turn, would soon become inflamed and that, thereafter, the rate of burning would depend largely upon the rate at which the now flaming droplet could both find the oxygen it required and be cleansed of its own combustion products; in other words, on its motion relative to the air. It would, of course, depend also on the size of the

liquid droplet. We expected, therefore, to find a condition somewhat analogous to that in a petrol engine; first a delay period while the envelope of vapour was being formed during which a substantial quantity of fuel had entered the cylinder, without any appreciable rise of pressure or temperature; this would be followed by a rapid rise in pressure when the accumulated droplets became fully inflamed and this, in turn, would be followed by a less rapid and more controllable rate of rise when the temperature was so high that the droplets would burn as they entered with very little delay indeed. We expected, therefore, to realize a pressure time diagram much as shown in figure 2, somewhere about half-way between the constant volume and the constant pressure cycle. Figure 3 shows an actual diagram taken later from a high speed sleeve valve Diesel engine.

It was clear at the outset that the two major problems before us were an investigation into the process of combustion and the design and development of a fuel injection system which would meter and time accurately the delivery of very minute quantities of liquid fuel, for it was quite obvious that the systems then in use on large slow running engines would not be applicable. Our first step was clearly the design and development of a fuel injection system which would be reasonably easy and cheap to produce in very small sizes, and which could be relied upon both to meter and time accurately the injection, at very high pressure, of minute quantities of liquid fuel of the order of 10 cu.mm., or even less per cycle and that at speeds of at least 2500 r.p.m., and higher if possible. This, though it looked a formidable problem, in fact proved to be very much easier than we had expected. I thought that the best way to tackle it would be to use an ordinary plunger pump with no packing but with very long sealing surfaces to prevent leakage, to give this pump relatively a very long stroke but to pick out for delivery only a small fraction from 0 to 10 % of the mid-portion of the stroke when the plunger was moving at its maximum velocity. This was effected by using two cam operated inlet valves and a single spring loaded delivery valve. Throughout the whole of the suction stroke of the pump, both inlet valves were held wide open. At the end of the suction stroke, one valve closed but the other was held open until nearly half-way up the delivery stroke. This was then also closed and the entrapped fuel delivered to the injector until, a little further up the stroke, the first valve was opened again, thus allowing the rest of the fuel to return to the suction side. Thus the time of start of injection was determined by the closing of one valve and the period and quantity delivered by the re-opening of the other. The timing of both valves was controlled by moveable taper wedges between the ends of the valve stems and the tappets. This pump worked well from the start and, although we had many teething troubles, due mostly to surging and aeration of the fuel, it remained practically unaltered for many years. Figure 4 shows this injection pump as fitted to a sleeve valve engine.

As would be expected with a pump of this type, the delivery per stroke tended to increase with increase of speed. This rising characteristic was very marked at low speeds but tended to flatten out at the higher speeds, owing to the elasticity of the fluid under very high pressure. We realized, of course, that this rising characteristic

would be a nuisance, in that, when idling, the engine would be unstable and, at any fixed setting of the pump, would tend either to run away or to peter out and stop. To cope with this instability, we developed a two-speed centrifugal, and later

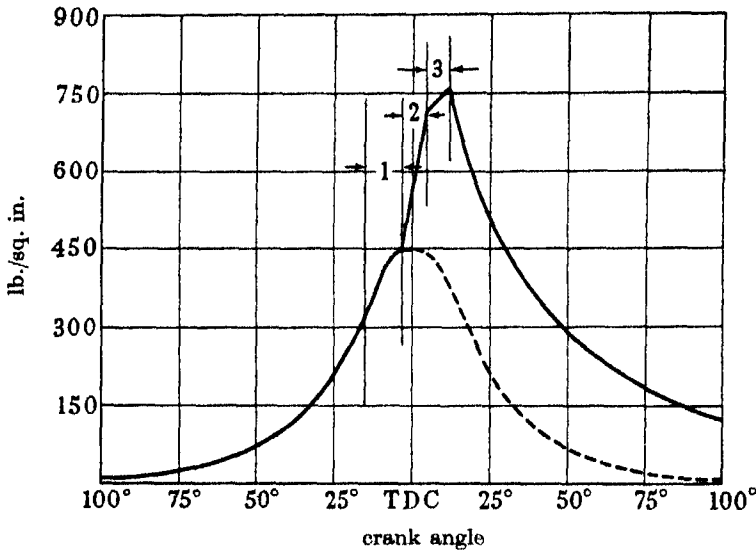


FIGURE 2. Diagram showing three phases of combustion process in compression ignition engine.

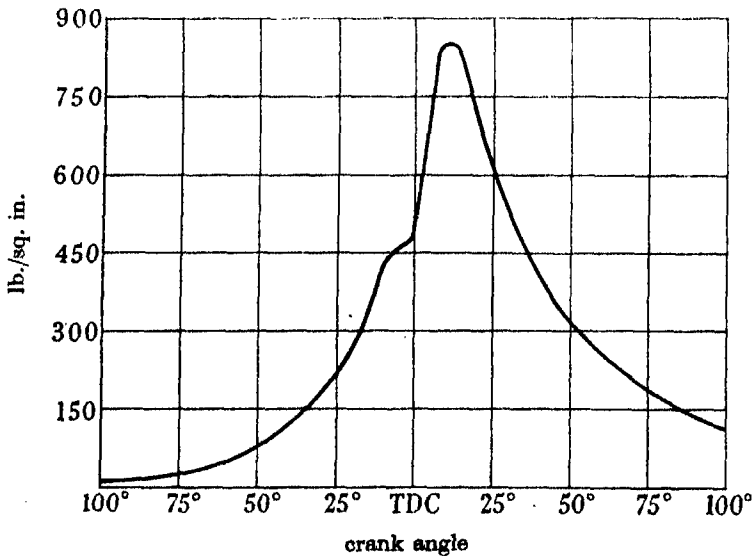


FIGURE 3. Single cylinder bore $5\frac{1}{2}$ in., stroke 7 in.; speed 2200 r.p.m.; b.m.e.p. 90 lb./sq. in., i.m.e.p. 122 lb./sq. in.; fuel consumption per b.h.p. hr. 0.39 lb., fuel consumption per i.h.p. hr. 0.285 lb.; piston speed 2570 ft./min.

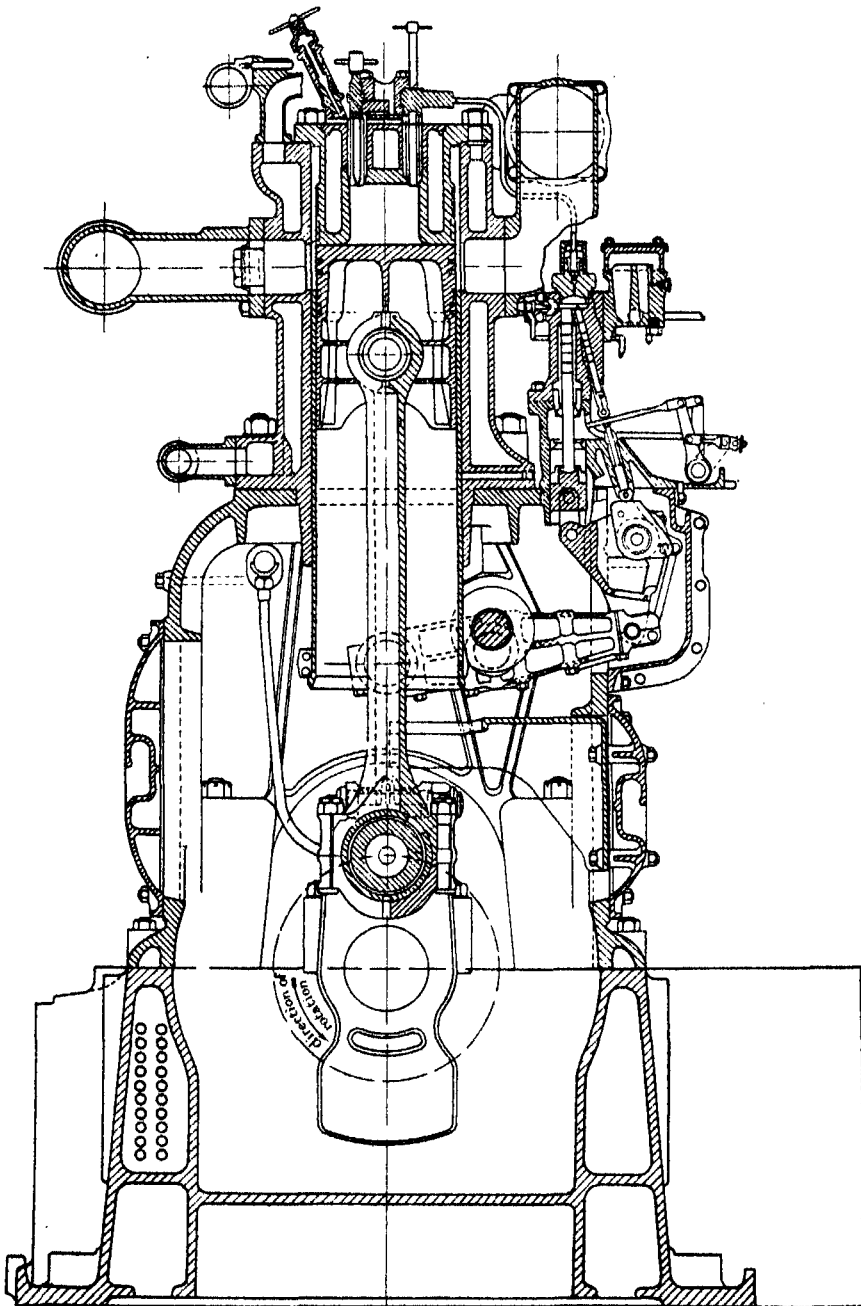


FIGURE 4. Arrangement of 7½ in. x 12 in. Brotherhood-Ricardo high speed Diesel engine (cross section).

a vacuum governor, the functions of which were to increase automatically the delivery of the pump whenever the engine speed fell below a certain pre-determined minimum, and to cut it off altogether when the limit of safe maximum speed was reached; between these two wide limits, the engine would be operated under direct hand or foot control.

Some years later, but quite independently, the Bosch Company of Stuttgart developed and, with prophetic foresight, went boldly into large scale production of a small high speed fuel injection pump employing the same principle, but of much neater and more compact form. Their pump, which employed also an almost identical governor mechanism, had only very short sealing surfaces and therefore required a far higher standard of workmanship and material to prevent leakage, but to this, they were accustomed. They certainly made a superb job of it and their injection pump, like their magneto before it, became a standard piece of equipment for all high speed Diesel engines. Had it been available five or six years earlier, it would have saved us a lot of time and trouble.

During this preparatory period, we had been experimenting with and trying to develop the single sleeve valve engine for high power aircraft use and had built several single cylinder experimental units which, as spark ignition engines, had given an excellent performance on petrol. We decided, therefore, to carry out our first running trials on the most robust of these units, which had already been calibrated very fully. The use of the sleeve valve was particularly attractive for our immediate purpose for several reasons, chief of which was that, since the cylinder head was encumbered with valves, we had complete freedom of manoeuvre as to the shape or form of combustion chamber.

Yet another important advantage, from an experimental point of view, was that with the admission of air to the cylinder through circumferential ports, we could, by means of external guide vanes, control the direction of entry and subsequent movement of the air within the cylinder. We had, in fact, already investigated this very fully during our previous research on petrol and found that we could, at will, obtain any condition ranging from indiscriminate turbulence to orderly rotational swirl.

For our first trial, we used the pump we had developed combined with an injector nozzle giving a very finely atomized cone shaped spray in a combustion chamber of conical form, and a compression ratio of 15:1, for our theories and in fact, all theories as to the process of combustion, pointed to the necessity of dividing the liquid fuel up into the smallest possible droplets, if we were to hope to get combustion completed in the very short time available. The engine started beautifully and ran very smoothly and steadily up to quite a high speed, but developed practically no power at all, in fact, only just enough to run itself round. Any attempt to increase the power output by delivering more fuel, resulted merely in the emission of dense clouds of black smoke from the exhaust and the deposition of masses of carbon in the cylinder.

Investigation revealed that, with very small fuel deliveries, combustion was both rapid and complete but that, at best, only about 15 to 20 % of the available

oxygen was combined; if more fuel was injected, all that happened was that the excess could not find the necessary oxygen. We concluded, therefore, that we were suffering from lack of penetration and that the spray was concentrated into a small local zone near the apex of the combustion chamber. We rang all the changes of air movement with but little effect and we varied the injection pressure and the rate of injection, also with very little effect, but, do what we would, we could not burn more than about 20 % of the available oxygen. We therefore decided to abandon the pulverizing type of injector and substitute one of the watering-can type; here we were faced with the difficulty that, in order to maintain the pressure needed for high penetration at low speeds, the holes, in a small engine, would have to be both few and very small. The smallest hole we could drill was about 0.2 mm. and the greatest number of this size we could use was about 6 or 8—these we spaced out at various angles designed to give as uniform a distribution of the fuel jets as possible.

With this new injector we at once obtained better results. We were able to burn twice as much fuel per cycle and to consume about 40 % of the available oxygen with at least a reasonably clean exhaust and that at a very high thermal efficiency. We found also, that the introduction of a moderate degree of orderly rotational air swirl was very effective in bringing more air into contact with the fuel jets, and so increasing the quantity of oxygen consumed. This was encouraging but still a long way off practical politics, for, to compete in power with the petrol engine, which can and does consume the whole of its oxygen, we, even with our much higher thermal efficiency, should have to be able to consume at least 75 %, and we were a long way off that. Also, we had incessant trouble with choking of the very small jets by minute particles of metal or scale, which somehow found their way through the best filters we could provide, and once a 0.2 mm. hole was blocked under a pressure of about 400 atmospheres, it was virtually impossible to clear it.

Although the change from a finely pulverizing to a multiple jet injector must have increased enormously the droplet size, yet there was no indication that we were suffering from unduly prolonged combustion even at speeds up to 2000 r.p.m.

These experiments, unpromising as they appeared, taught us much, for we had learned that rate of burning of the fuel droplets was not a limiting factor, that large variations in the coarseness of the spray particles had surprisingly little effect, and in short, that the more urgent problem was how to bring the fuel and air into contact with each other in the short time available.

We decided, therefore, as a next step, to go right to the other extreme, to employ a single hole injector of the plain fire hose type giving the maximum possible penetration quite regardless of pulverization. We had started with a scent spray, had done better with a watering can; the next step was to try a fire hose. At the same time it was, of course, obvious that to bring the air into contact with a single column of liquid, we should require a controlled but very intense air movement; the ideal being that the whole of the air within the combustion chamber should be made to sweep once past the jet of fuel during the injection period.

We therefore constructed a new combustion chamber of cylindrical form, the diameter being about half that of the piston and the height rather less, and we arranged our air entry vanes to give a rotational swirl about the axis of the cylinder. We also brought our piston into very close contact with the flat annular portion of the cylinder head in order both to reduce as far as possible the volume external to the main combustion chamber and at the same time to produce, by 'squish', a forced vortex in the chamber. In the top and to one side of this cylindrical chamber and at about the radius of gyration, we fitted our single hole injector squirting straight downwards (see figure 5). The result was an immediate and striking improvement; at once we obtained nearly double the power we had reached before and we were able to run to the maximum speed of which the engine was capable. Indicator diagrams of the pressure changes in the cylinder showed that combustion was extremely rapid and this was confirmed by the observation that the indicated thermal efficiency actually increased with increase of speed up to the highest speed of which the engine was capable—about 2300 r.p.m.

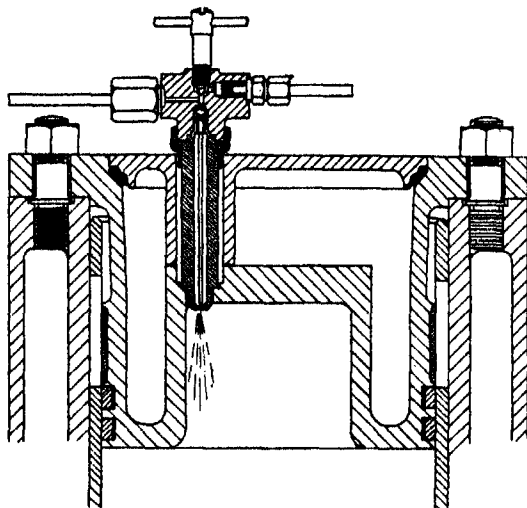


FIGURE 5

Next we found that by bringing the injector nearer and nearer to the side of the combustion chamber, we gained progressively more power, until a critical point was reached when the spray actually impinged against the side wall.

We had, at last, achieved some really encouraging results and felt that the next step was to explore more thoroughly the air movement in the combustion chamber. To this end we developed a small anemometer which could be fitted inside the combustion chamber to record, at least in relative terms, the speed of rotation of the air within the chamber. This, of course, could be used only when the engine was motored without any fuel.

We found also that by painting the inside of the combustion chamber and the crown of the piston with a white enamel paint, allowing it nearly to dry and then running the engine for a few seconds under power, we could get clear-cut markings both of the air movement, of the impingement, if any, of the fuel jet against the crown of the piston and also some indication of the temperature distribution. Thus, we learned that even with a plain fire hose jet and a fuel injection pressure of about 300 atmospheres, the penetration in an air density of 15 atmospheres was only just sufficient to reach the piston crown, a matter of less than 2 in. It appeared also that no matter how intense the air swirl, the main core of the jet was but little deflected while the whiskers of spray were carried inwards towards the centre of the chamber. Our anemometer now proved most valuable, in that it enabled us to calibrate our external guide vanes in terms of air swirl, which latter we defined as the ratio of air to crankshaft revolutions. It proved also that for any given setting, this ratio remained practically constant over the whole speed range.

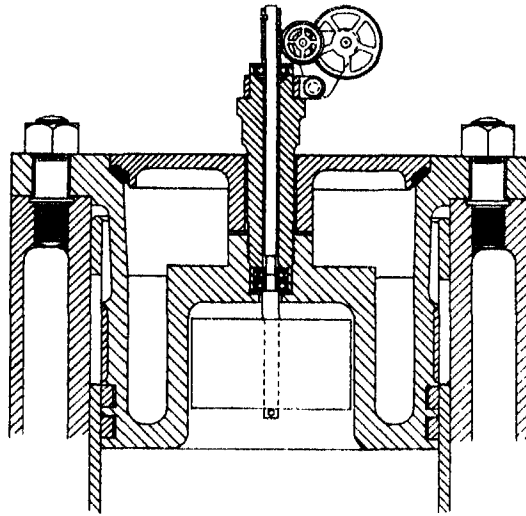


FIGURE 6. Ricardo swirl meter.

Figure 7 shows the striking effect on power and efficiency made by varying the air swirl and it will be seen that the optimum performance was obtained when the ratio was between 9 and 10:1 that is to say, when the anemometer within the combustion chamber made nine revolutions during one of the crankshaft. The true air speed must, of course, have been considerably higher than this, owing to the friction, inertia and slip of the anemometer.

Under the optimum conditions as to swirl, we were able to combine over 70 % of the available oxygen and so, with our higher thermal efficiency, to develop about 85 % of the power obtained from the same engine on petrol, and that with an indicated thermal efficiency of approximately 52 %, quite an encouraging performance.

We had now satisfied ourselves on several important points, viz. that engine speed need not be limited by rate of burning, that penetration of the fuel jet was of far more importance than fine pulverization, and lastly, that it was far easier and more effective to bring the air to meet the fuel than the fuel to meet the air. I had become wedded, too, to the practical advantages both of a single hole orifice with its freedom from choking, and to the use of an intense air swirl not only as a means of bringing the air into contact with the fuel stream, but also for the no less important function of wiping the dew drop from the nose of a dribbling injector; it was clear, however, that so long as we stuck to the single hole injector, we should have to employ a very intense air swirl. This was easy enough to obtain in a sleeve valve engine but not so easy in a poppet valve.

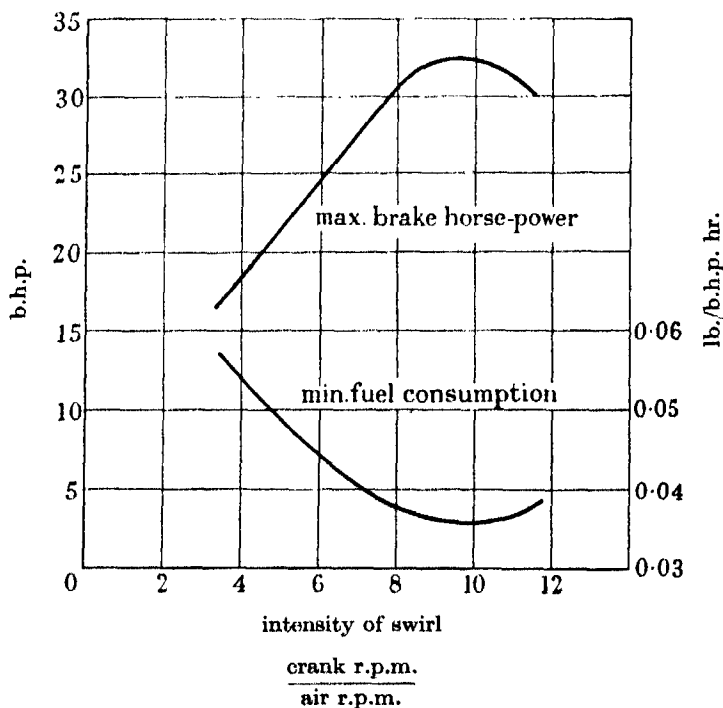


FIGURE 7

As I have said earlier, our ultimate goal was the development of an engine for road transport, but for various reasons, we did not consider the sleeve valve suitable for this service and the one form of combustion system we had developed so far was applicable only to a sleeve valve engine. I had, however, pinned my faith to the sleeve valve where high sustained power was required, as in the case of aircraft and heavy duty industrial engines. It was decided, therefore, to proceed with the sleeve valve Diesel both as an aero-engine and as a heavy duty industrial engine and at the same time to try and evolve from the lessons we had learned, a poppet valve

version for road transport. This latter looked like being a far more difficult problem for, with the very high ratio of compression, and consequent small clearance space the only possible position for the valves was vertically in the cylinder head, and, with this geographical layout, there was no hope of getting adequate air swirl during the air admission stroke. The obvious alternative, therefore, was to try and create an intense swirl during the compression stroke, by compressing the air into a separate chamber communicating by a tangential passage and to do this with the minimum possible loss of heat during transfer in or out. For road service, there was also another very important factor to be taken into account, namely, the smell of the exhaust. With our sleeve valve engines, we had succeeded in getting a completely smokeless and invisible exhaust, but it had a very pungent smell due mainly to the presence of aldehydes. During our research on fuels, we had found from sampling tests, that aldehydes and other products of partial combustion, were stabilized when the flame impinged upon a relatively cool surface. With these considerations in mind, we decided to experiment with a separate spherical combustion chamber communicating with the cylinder via a tangential passage and, in order to reduce both heat losses and smell, we made the lower half of this chamber, containing the passageway, as a separate member, heat insulated from the rest of the cylinder. Thus it attained a very high temperature somewhere about midway between the two extremes of the cycle, while the temperature of its surface against which the flame impinged, was too high to permit of the stabilization of the products of partial combustion.

For our earlier experiments in a poppet valve engine, we mounted the fuel injector in a spherical trunnion so arranged that we could site the spray in any direction within the sphere.

This arrangement promised well right from the start. We spent a lot of time exploring the optimum area of passageway to give the swirl ratio we needed and in finding the best direction of the spray which proved to be not straight across the diameter but somewhat tangentially in a downstream injection. Once we had found the optimum conditions, we obtained an extremely good power output, and were able to combine up to 80 % of the oxygen content and so obtain a power output very nearly equal to that of the same engine on petrol. Compared with our sleeve valve engine results, we were getting about 10 to 15 % more power but, owing to the higher heat losses, our specific consumption was about 5 to 10 % greater, though still little more than half that of a contemporary petrol engine, when both were running under road service conditions. Figure 8 shows an experimental poppet valve engine with separate swirl chamber.

We found also, as we had hoped, that the heat insulated member served another and very useful purpose in that its rise of temperature with increase of engine speed or load, by raising the compression temperature, compensated for the varying delay period of the start of burning and so allowed us to work at all speeds or loads with a fixed injection timing, a great advantage from a mechanical point of view.

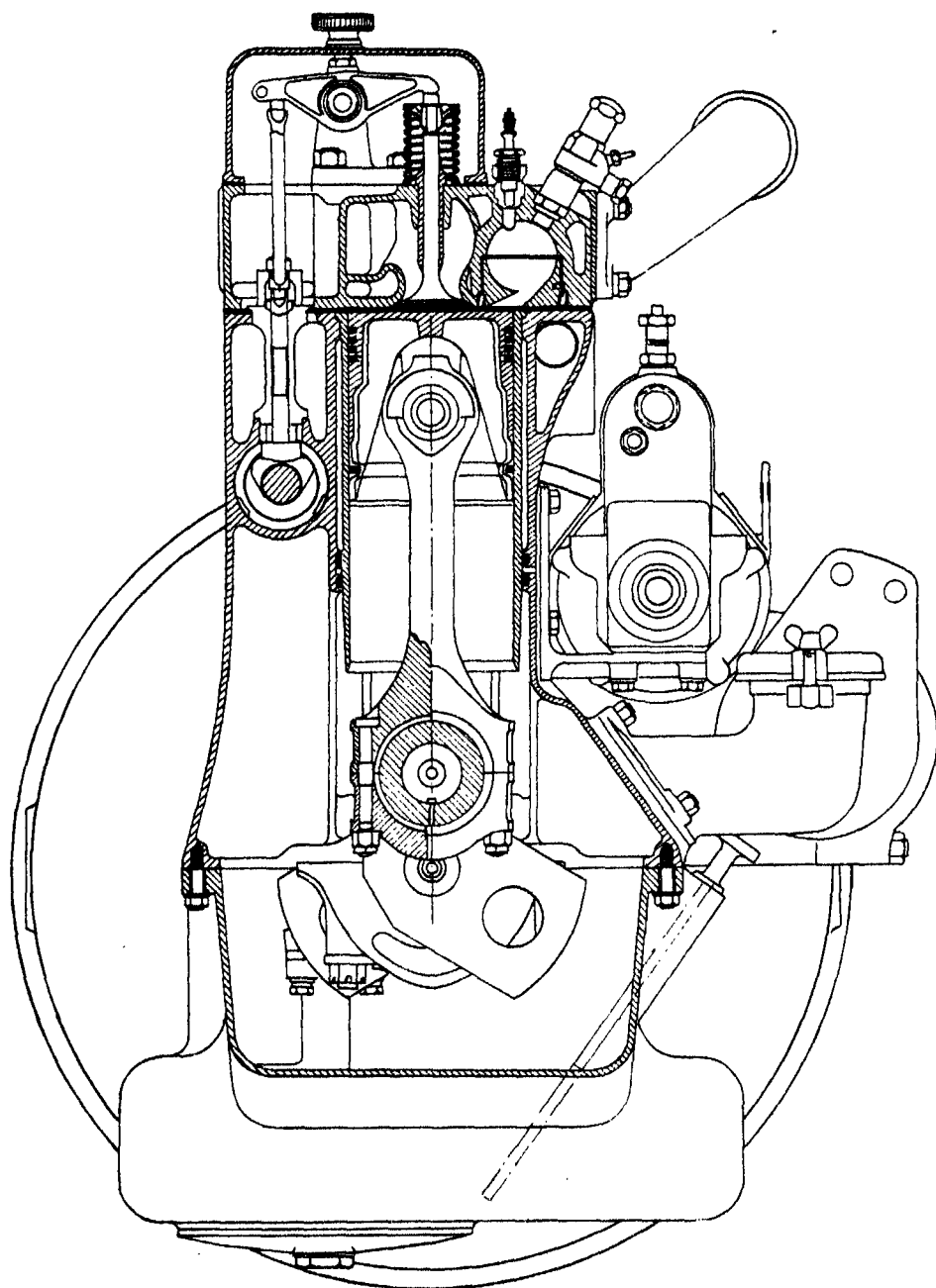


FIGURE 8. Cross section arrangement of 6 cylinder compression ignition engine $4\frac{1}{2}$ in. bore, $5\frac{1}{2}$ in. stroke.

By this time, we felt that we had gained sufficient experience to justify our issuing designs and working drawings of a sleeve valve version for uses other than road service, and also to attempt the design of a full scale Diesel aero-engine. Messrs Brotherhood were the first to manufacture and market a range of industrial engines to our designs followed by Messrs Mirrlees Bickerton and Day. These were of comparatively large size, viz. 50 h.p. per cylinder with numbers of cylinders ranging from one to eight and developing up to 400 h.p. These proved successful and became very popular, more especially for cases where the duty was very arduous, such, for example, as electric generating plants, pumping stations, and as auxiliary engines on board ship.

Figure 9, plate 4 illustrates a six cylinder sleeve valve engine as made by Messrs Mirrlees Bickerton and Day designed for direct coupling to either a dynamo or centrifugal pump.

Our next venture was the design and construction of a 300 h.p. Diesel aero-engine. In this, both Rolls Royce and the Royal Aircraft Establishment co-operated most generously; in fact, we built simultaneously, two identical sleeve valve aero-engines, one petrol and one Diesel.

On test, the Diesel (see figure 10, plate 4) developed 330 h.p. at 2300 r.p.m. and the petrol version 370 h.p. while both engines weighed a fraction over 700 lb. The specific consumption of the Diesel was 0.41 lb. per b.h.p. hour and of the petrol 0.6 lb.—a very favourable comparison—but about this time, vast improvements were taking place in the processing and octane number of aviation spirit. By taking immediate advantage of these we were able, by supercharging, to step up the power of the petrol version from 370 to very nearly 700 h.p. at a cost of only 50 lb. additional weight, but owing to the high gas pressures, our slender margin of safety did not permit of the Diesel version being supercharged and the comparison thus soon became an odious one. Since then, synthetic aviation spirit has further improved, thus permitting both of higher ratios of compression with correspondingly lower fuel consumption and the use of a still heavier supercharge, with the result that the Diesel has now been left far behind in the race for the air.

While our experimental Diesel aero-engine came to nothing as such, yet the effort was by no means wasted, for we learned a great deal from the attempt to make an ultra-light and, for that date, an ultra-high-speed Diesel engine, while the engine itself, though it never flew, later performed yeoman service in a racing car driven by Capt. Eyston and captured a number of world records.

Although by this time we were getting a very satisfactory performance from the poppet valve version, we still had many mechanical problems to cope with before we could put it forward as a vehicle engine.

When at last we did feel ready, its immediate success was rather unexpected and embarrassing. The new engines of which figure 11, plate 4 shows the first prototype did just double the mileage per gallon in London service and proved about 60 % better than the petrol engines on long hauls, and, perhaps more important still, their drivers were enthusiastic about their ease of handling and

general behaviour, with the result that, in a very short time, we were besieged by nearly forty different manufacturing firms all wanting data and designs and our thoughts and hands for the next few years were completely occupied in getting out designs and in struggling, against time, to solve the outstanding mechanical problems. We did make some further improvements on the combustion side, which gave us a further increase in power and efficiency, but our main efforts were directed to locating and strengthening the weak links in the mechanical chain.

Meanwhile, others and notably Messrs Gardner's who, in friendly rivalry, had taken up the same line of development and, starting with relatively stagnant air and multi-hole orifices in an open combustion chamber, had succeeded, by heroic efforts, in mastering the filtration problem to the extent that they no longer suffered seriously from choked jets. They, too, had found that, by introducing a modest degree of air swirl, which could be obtained by masking a portion of the inlet valve circumference, they could use fewer and larger orifices. By such means they were able to reduce the convection heat losses and so obtain a higher overall efficiency but at a considerable cost in power. Compared with the single jet swirl chamber type, these open chamber engines were able to show from 5 to 10 % lower fuel consumption but at a cost of from 15 to 20 % in power output, from the same size and weight of engine. To-day, broadly speaking, all high speed Diesel engines built in this country, are either of the swirl or open chamber type. We prefer the former when the accent is on power, and the latter when it is on fuel economy.

So rapid was the turnover from petrol, that during the last six years before the 1939-1945 War, over 20,000,000 h.p. of Diesel engines were placed on the road in this country alone. This changed completely the economic picture so far as the oil companies were concerned, for Diesel fuel became in shorter supply than petrol, and our efforts to-day are directed towards using the still heavier distillates and residue oils.

Thus far, I have spoken only of our problems in connexion with the fuel admission and combustion which proved fairly simple and straightforward. Much more difficult were the purely mechanical and plumbing problems which grew in magnitude and diversity as our power output improved.

Of these, the chief headaches were excessive cylinder wear, overheated pistons, cracking of cylinder heads, bearing failures, etc.

The problem of cylinder wear in internal combustion engines had long been a baffling one, on account both of its inconsistency and of the peculiar form it took, namely, that of a deep groove in the bore at the point where the top piston ring came to rest at the top of its stroke. The popular belief that wear was caused by abrasion due to the introduction of dust, etc. with the entering air, just wouldn't hold water. It would neither explain the extremely localized nature of the wear nor the fact that marine engines operating in a dust free atmosphere suffered at least as severely, nor would it explain the puzzling observation that single sleeve valves, though made of the same material, showed negligible wear.

For long I had suspected that chemical corrosion was at least a contributory cause. Our earlier sampling tests from the combustion chamber of an engine had revealed the presence in and ahead of the actual flame front, of traces of various organic acids, such as formic acid and, though they appeared to be but the transient products of partial combustion, I was deeply suspicious of them. In an attempt to fit the observed facts, I formed the theory that, at the moment when the piston ring came to rest at the top of its stroke with the full gas pressure behind it, only boundary, as opposed to fluid, lubrication separated it from the cylinder wall and that, under these conditions, the protecting film of oil would be of no more than molecular thickness and might locally be broken down altogether; as the piston ring gathered way on its downward stroke, it would soon ride up again on a fluid film, but would leave behind it a narrow band of unprotected metal exposed to attack just at the moment when the concentration of partial products was at its maximum, and that the attack would be most virulent if the surface temperature was below the dew point of the products in question. This theory might explain the extremely localized nature of the wear and the absence of similar wear in the sleeve valve engine since, with the combined movement of the sleeve and piston, relative motion between the two never ceased and full fluid lubrication might be maintained at all times. We tried to obtain some positive evidence to support this theory by attempts to stop an engine suddenly in mid-career, whip off the cylinder head and find, as I hoped to find, a dry and perhaps rusty band, but, do what we would, we could not stop an engine quickly enough to prevent the evidence being wiped away by a subsequent stroke of the piston. Some time later, an accident produced just the evidence I was in search of. When testing a single cylinder engine, the base of the cylinder fractured suddenly, with the result that the whole cylinder flew off and landed on the concrete floor where it broke into several pieces. On examining these pieces within a couple of minutes of the failure, we found that the whole length of the liner was well lubricated with the exception of a narrow, dry and already rusty band at the point where the top piston ring came to rest.

Meanwhile, acting on the corrosion theory, both the Automobile Research Association and ourselves experimented with corrosion resisting materials such as stainless steels and irons for the cylinder liner, but we found that none of these would mate with the piston rings to form a mutual bearing surface; we did, however, have some success with a high phosphorous cast iron which showed about half the rate of wear of a normal iron. Later, we found that certain stainless steels could be surface treated by nitrogen hardening to form a good bearing surface and these were almost immune from wear, but both the material and the treatment were very costly. We tried, of course, all manner of electro-deposited linings, but only chromium appeared at all hopeful; the snag with this was that the surface soon attained a very high polish upon which the oil would not spread, with the result that piston seizures were liable to occur, with disastrous consequences. Later, Van der Horst, a Dutch expert on electro-plating, suggested the possibility of a thick deposit of porous chromium obtained by very rapid deposition. This, when tried, proved very promising

at first, but we found that after several hundred hours running, the surface was sometimes liable to acquire a high polish when piston seizure followed. Later, a new technique was evolved by Van der Horst which seems, so far, to be entirely satisfactory. This consists in first depositing a thick layer of chromium as before, machining this to its final dimension by grinding and honing, and then replacing the finished liner in the plating bath but with the polarity reversed, thus stripping from the finished surface a minute quantity of metal. This leaves the surface covered with very minute but deep pits which serve to give the oil film a foothold.

I cannot pretend that even to-day the problem of cylinder wear is solved, but it has been reduced to tolerable proportions by fitting thermostats in the water circulation in order as quickly as possible to bring the temperature of the liner above the dew point, and by the use of high phosphorous cast iron liners which are cheap and easy to renew or regrind, or by the use, when the price will run to it, of either nitrided stainless steel or Van der Horst chromium plated liners, both of which are expensive initially, but almost everlasting.

From my earliest days I had been taught that owing both to its higher thermal efficiency and lower mean cycle temperature, the flow of heat to the pistons, cylinders and exhaust valves in a Diesel engine was much less than in a petrol engine. It was a bitter disappointment therefore to find that while the exhaust valves and cylinder barrels were no longer a source of worry, the pistons and cylinder heads, on the other hand, ran very much hotter, and we at once ran headlong into all the troubles such as gummed up piston rings, cracked or seized pistons and cracked cylinder heads, which we associate with overheating—indeed, it was rather a shock to find that the piston of a Diesel engine reached the same temperature as that of a petrol engine when it was developing only about half the power.

Although the *mean* temperature of combustion is lower and the mean cycle temperature very much lower, yet in the Diesel the actual temperature is both very high and very localized, while the rate of heat transfer to the piston and cylinder head, due both to the high density and intense convection is much greater than in a petrol engine.

The mechanism of heat transfer from the crown of the piston to the cylinder walls is still a little obscure, but all temperature gradient measurements indicate that the bulk of the heat is transmitted via the piston rings. In large Diesel engines the pistons are hollow and water or oil cooled as a matter of course, but in a small high speed engine the problem of liquid cooling the pistons is a very formidable one. The only alternative was to increase the heat path by thickening greatly the aluminium in both the crown and the upper part of the skirt and by adding more piston rings merely for purposes of heat transfer. By so doing, we increased substantially both the dynamic forces due to the inertia of pistons and the internal friction. To cope with the dynamic forces, as also with the somewhat higher gas pressures, we had both to increase the rigidity of the engine structure and to enlarge and stiffen all the bearings.

Other tiresome difficulties have been caused by cracking of cylinder heads due to localized and unequal heat flow. By plotting temperature gradients through the metal, we were able to identify the zones of intense heat flow and, in most cases, to cope with them either by appropriate distribution of the metal or by directing the flow of the cooling circulation, or both.

Again, crankshaft torsional vibration proved very troublesome. This worry has been with us always, but was very much more acute in the Diesel engine, due to the high compression and to the heavier pistons. The well-known Lanchester damper will cope with most cases of torsional vibration in the petrol engine, but will not stand up to the Diesel; we had, therefore, to employ much larger diameter and stiffer crankshafts and, in some cases, to resort to the use of pendulum dampers and other methods of de-tuning.

Yet again, owing to the large diameter crankshaft bearings we were compelled to use, the rubbing velocity became so high and the heat generated by friction so great, that the ordinary anti-friction linings broke down. To combat this, we had to increase greatly the flow of cooling oil through the bearings but this, in turn, led us into difficulty with excessive oil passing the pistons. We came to the conclusion, therefore, that since only a small amount of oil is required for lubrication as such, and a very large quantity for cooling, it would be better to separate the two functions and to cool the crankshaft internally by flushing it through from end to end with a copious flow of oil. This proved very easy and simple to apply in practice (see figure 12).

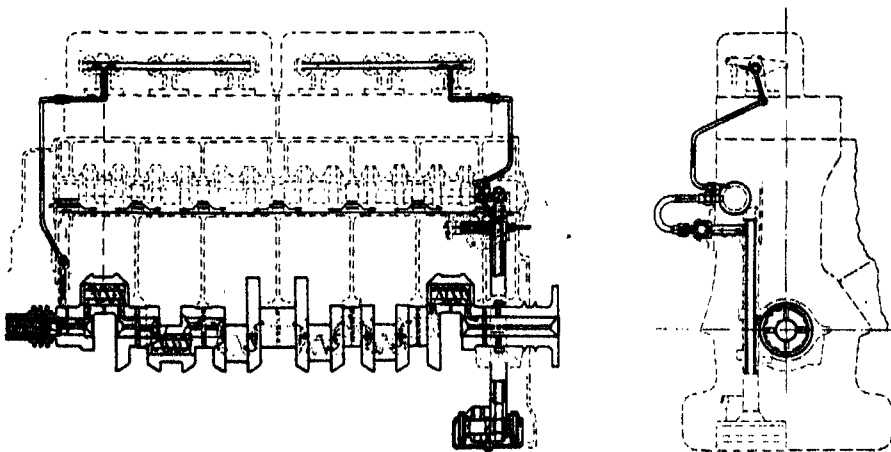


FIGURE 12. Lubricating arrangement of 6 cylinder compression ignition engine.

All these and many other mechanical problems proved far more elusive and difficult than any connected with the combustion system; moreover, they were not so soon apparent, but reared their ugly heads progressively as the combustion system and therefore the power output improved. To mechanical problems such

as these, there is never any end for, so soon as they have been mastered, a new set of conditions arises, a higher speed, or a lower weight is demanded and a new crop at once appears.

We had never been under any illusion that a petrol engine could satisfactorily be converted into a Diesel by merely changing over a few parts, except for purely experimental purposes; in fact, when fully developed, they share scarcely one single part in common.

Despite these and many other mechanical difficulties, the high speed Diesel engine of to-day is at least as reliable, in some respects much more so, than the petrol engine and is now in almost universal use for all forms of heavy road transport both here and on the Continent.

I have tried, as briefly as possible, to describe a piece of research and development work which has extended over nearly 30 years, but have only been able to deal with the more prominent features of it. The combustion problems, which looked so formidable at the start, presented really surprisingly little difficulty and, once overcome, they did not recur. Far otherwise was it with the mechanical problems which cropped up anew at every turn, while the solution of one problem frequently gave birth to another.

In conclusion, I would like to emphasize once again how much we owed to the valuable advice and generous help which was always forthcoming from all quarters, in our hours of need. In particular, we owe a deep debt of gratitude to the metallurgical industry in general, who not only gave us invaluable advice, but went to endless trouble to produce for us the materials we needed.

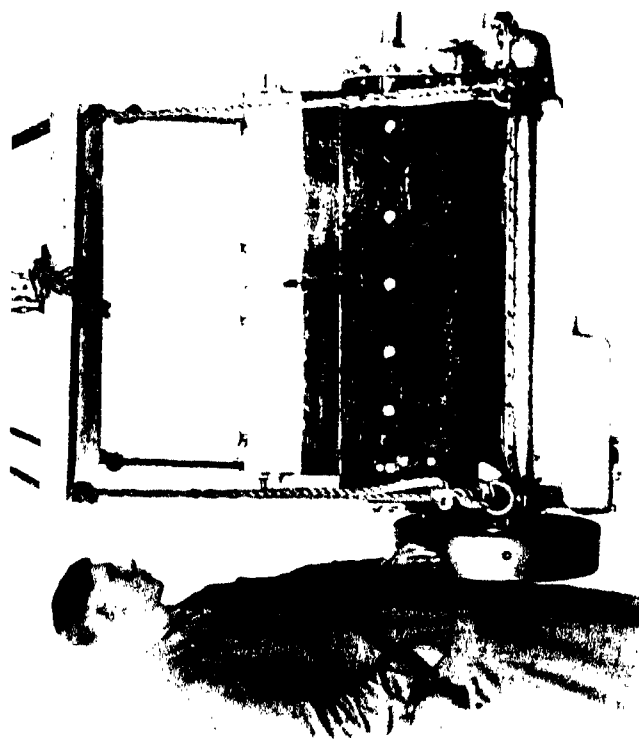


FIGURE 11

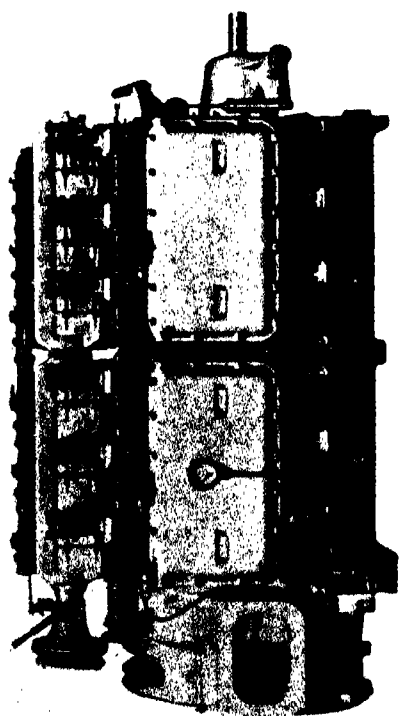


FIGURE 9

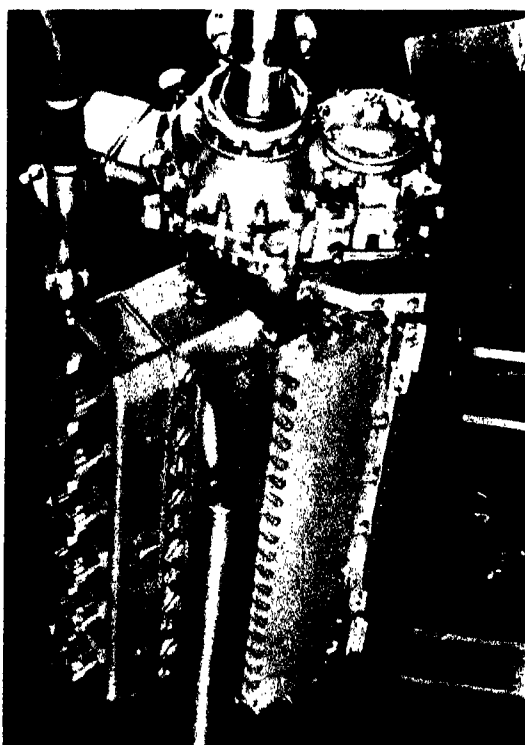


FIGURE 10

Three-dimensional stress systems in isotropic plates. II

BY A. E. GREEN AND T. J. WILLMORE

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The problem of an isolated force uniformly distributed through a plate of finite thickness and acting parallel to the faces of the plate, which are free from applied stress, is solved in integral form. Numerical work is carried out for the average values of the stresses in order to compare the results with those found from the approximate theory of generalized plane stress. In addition, numerical values of the stresses are found on the faces of the plate and on the plane midway between the faces.

1. INTRODUCTION

It was pointed out in a previous paper (Green 1948), referred to subsequently as paper I, that the accuracy of the usually accepted theory of generalized plane stress in a plane plate can only be tested satisfactorily by comparing the results obtained from the theory with those found from three-dimensional solutions of the elastic equations when no simplifying physical assumptions are made, such solutions having also, of course, considerable interest in themselves. The problem solved in paper I was one of stress concentration at a circular cylindrical hole in a plate under uniform tension. In the present paper the problem discussed is that of an isolated force uniformly distributed through a plate of finite thickness and acting parallel to the faces of the plate which are free from applied stress. This problem has only limited physical interest, but the mathematical analysis is much simpler than for the stress concentration problem and a fairly comprehensive picture of the stress distribution can be obtained with relatively little numerical work.

2. FUNDAMENTAL EQUATIONS

In rectangular co-ordinates the equations of equilibrium of a homogeneous isotropic elastic solid, when body forces are absent, are

$$\left. \begin{aligned} \frac{\partial \bar{x}\bar{x}}{\partial x} + \frac{\partial \bar{x}\bar{y}}{\partial y} + \frac{\partial \bar{x}\bar{z}}{\partial z} &= 0, \\ \frac{\partial \bar{x}\bar{y}}{\partial x} + \frac{\partial \bar{y}\bar{y}}{\partial y} + \frac{\partial \bar{y}\bar{z}}{\partial z} &= 0, \\ \frac{\partial \bar{x}\bar{z}}{\partial x} + \frac{\partial \bar{y}\bar{z}}{\partial y} + \frac{\partial \bar{z}\bar{z}}{\partial z} &= 0. \end{aligned} \right\} \quad (2.1)$$

The components of stress $\bar{x}\bar{x}, \dots, \bar{y}\bar{z}$ are given in terms of the displacements (u_x, u_y, u_z) by the equations

$$\left. \begin{aligned} \bar{x}\bar{x} &= \lambda\Delta + 2\mu e_{xx}, & \bar{y}\bar{z} &= \mu e_{yz}, \\ \bar{y}\bar{y} &= \lambda\Delta + 2\mu e_{yy}, & \bar{z}\bar{x} &= \mu e_{zx}, \\ \bar{z}\bar{z} &= \lambda\Delta + 2\mu e_{zz}, & \bar{x}\bar{y} &= \mu e_{xy}, \end{aligned} \right\} \quad (2.2)$$

where

$$\Delta = \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z}, \quad (2.3)$$

and the strain components $e_{xx}, \dots, e_{yz}$ are given by equations of the type

$$e_{xx} = \frac{\partial u_x}{\partial x}, \quad e_{yz} = \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y}. \quad (2.4)$$

If the expressions (2.2) are substituted in (2.1) it is found that the displacements satisfy the equations

$$\left. \begin{aligned} \mu \nabla^2 (u_x, u_y, u_z) + (\lambda + \mu) \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \Delta &= 0, \\ \nabla^2 \Delta &= 0. \end{aligned} \right\} \quad (2.5)$$

In discussing stress distributions in plane plates Dougall (1904) used certain types of solutions of (2.5) of which some use will be made here. A possible set of displacements which satisfy (2.5) is

$$\left. \begin{aligned} u_x &= \frac{\partial \omega}{\partial x} + \alpha \frac{\partial \phi}{\partial x} + 2z \frac{\partial^2 \phi}{\partial x \partial z}, \\ u_y &= \frac{\partial \omega}{\partial y} + \alpha \frac{\partial \phi}{\partial y} + 2z \frac{\partial^2 \phi}{\partial y \partial z}, \\ u_z &= \frac{\partial \omega}{\partial z} - \alpha \frac{\partial \phi}{\partial z} + 2z \frac{\partial^2 \phi}{\partial z^2}, \\ \Delta &= 2(1 - \alpha) \frac{\partial^2 \phi}{\partial z^2}, \end{aligned} \right\} \quad (2.6)$$

where ω, ϕ are harmonic functions, i.e. they satisfy the equation

$$\nabla^2 (\omega, \phi) = 0. \quad (2.7)$$

The constant α in equation (2.6) is defined by the relations

$$\alpha = (\lambda + 3\mu)/(\lambda + \mu) = 3 - 4\eta, \quad (2.8)$$

where η is Poisson's ratio.

In the present paper it is more convenient to use cylindrical polar co-ordinates (r, θ, z) , and the displacements (u_r, u_θ, u_z) can be found from (2.6). Thus

$$\left. \begin{aligned} u_r &= \frac{\partial \omega}{\partial r} + \alpha \frac{\partial \phi}{\partial r} + 2z \frac{\partial^2 \phi}{\partial r \partial z}, \\ u_\theta &= \frac{1}{r} \frac{\partial \omega}{\partial \theta} + \frac{\alpha}{r} \frac{\partial \phi}{\partial \theta} + \frac{2z}{r} \frac{\partial^2 \phi}{\partial \theta \partial z}. \end{aligned} \right\} \quad (2.9)$$

In terms of (u_r, u_θ, u_z) the strains are

$$\left. \begin{aligned} e_{rr} &= \frac{\partial u_r}{\partial r}, \quad e_{\theta\theta} = \frac{1}{r} \frac{\partial u_\theta}{\partial \theta} + \frac{u_r}{r}, \quad e_{zz} = \frac{\partial u_z}{\partial z}, \\ e_{rz} &= \frac{1}{r} \frac{\partial u_z}{\partial \theta} + \frac{\partial u_\theta}{\partial z}, \quad e_{rz} = \frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}, \quad e_{r\theta} = \frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r} + \frac{1}{r} \frac{\partial u_r}{\partial \theta}, \end{aligned} \right\} \quad (2.10)$$

and the stresses are related to the strains by the equations

$$\left. \begin{aligned} \widehat{rr} &= \lambda\Delta + 2\mu e_{rr}, & \widehat{\theta z} &= \mu e_{\theta z}, \\ \widehat{\theta\theta} &= \lambda\Delta + 2\mu e_{\theta\theta}, & \widehat{rz} &= \mu e_{rz}, \\ \widehat{zz} &= \lambda\Delta + 2\mu e_{zz}, & \widehat{r\theta} &= \mu e_{r\theta}. \end{aligned} \right\} \quad (2.11)$$

From (2.6), (2.9), (2.10) and (2.11) it is found that

$$\left. \begin{aligned} \frac{\widehat{rr}}{2\mu} &= \frac{\partial^2 \omega}{\partial r^2} + \alpha \frac{\partial^2 \phi}{\partial r^2} + 2z \frac{\partial^2 \phi}{\partial z \partial r^2} + (\alpha - 3) \frac{\partial^2 \phi}{\partial z^2}, \\ \frac{\widehat{\theta\theta}}{2\mu} &= \frac{1}{r} \frac{\partial \omega}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \omega}{\partial \theta^2} + \frac{\alpha}{r} \frac{\partial \phi}{\partial r} + \frac{\alpha}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} + \frac{2z}{r} \frac{\partial^2 \phi}{\partial z \partial r} + \frac{2z}{r^2} \frac{\partial^2 \phi}{\partial z \partial \theta^2} + (\alpha - 3) \frac{\partial^2 \phi}{\partial z^2}, \\ \frac{\widehat{zz}}{2\mu} &= \frac{\partial^2 \omega}{\partial z^2} - \frac{\partial^2 \phi}{\partial z^2} + 2z \frac{\partial^2 \phi}{\partial z^3}, \\ \frac{\widehat{\theta z}}{2\mu} &= \frac{1}{r} \frac{\partial^2 \omega}{\partial \theta \partial z} + \frac{1}{r} \frac{\partial^2 \phi}{\partial \theta \partial z} + \frac{2z}{r} \frac{\partial^2 \phi}{\partial \theta \partial z^2}, \\ \frac{\widehat{rz}}{2\mu} &= \frac{\partial^2 \omega}{\partial r \partial z} + \frac{\partial^2 \phi}{\partial r \partial z} + 2z \frac{\partial^2 \phi}{\partial r \partial z^2}, \\ \frac{\widehat{r\theta}}{2\mu} &= \frac{1}{r} \frac{\partial^2 \omega}{\partial r \partial \theta} - \frac{1}{r^2} \frac{\partial \omega}{\partial \theta} - \frac{2z}{r^2} \frac{\partial^2 \phi}{\partial z \partial \theta} + \frac{2z}{r} \frac{\partial^2 \phi}{\partial z \partial r \partial \theta} + \frac{\alpha}{r} \frac{\partial^2 \phi}{\partial r \partial \theta} - \frac{\alpha}{r^2} \frac{\partial \phi}{\partial \theta}. \end{aligned} \right\} \quad (2.12)$$

3. THE ISOLATED FORCE PROBLEM

Consider now a plate of infinite extent and of uniform thickness $2h$, bounded by the planes $z = \pm h$. An isolated force of intensity P per unit length is directed along the axis of x and is situated along the z axis from $z = -h$ to $z = +h$.

If h is very large the problem is the ordinary one of plane strain and the solution is well known (Love 1927, p. 209). The displacements in this case are*

$$\left. \begin{aligned} u_r &= -\frac{P}{4\mu\pi} \left\{ \frac{3-4\eta}{2(1-\eta)} \log r - \frac{1}{2(1-\eta)} \right\} \cos \theta, \\ u_\theta &= \frac{P}{4\mu\pi} \left\{ \frac{3-4\eta}{2(1-\eta)} \log r \right\} \sin \theta, \\ u_z &= 0, \end{aligned} \right\} \quad (3.1)$$

and the stresses are

$$\left. \begin{aligned} \widehat{rr} &= -\frac{P}{4\pi} \frac{(3-2\eta) \cos \theta}{(1-\eta)r}, & \widehat{zz} &= -\frac{P\eta \cos \theta}{2\pi(1-\eta)r}, \\ \widehat{\theta\theta} &= \frac{P}{4\pi} \frac{(1-2\eta) \cos \theta}{(1-\eta)r}, & \widehat{r\theta} &= \frac{P}{4\pi} \frac{(1-2\eta) \sin \theta}{(1-\eta)r}, \end{aligned} \right\} \quad (3.2)$$

with $\widehat{rz}$ and $\widehat{\theta z}$ both zero. The corresponding 'generalized plane stress' solution for the average values of the stresses is obtained from the plane strain solution by replacing η by $\sigma = \eta/(1+\eta)$ with the exception that the stress $\widehat{zz}$ is omitted.

* These differ by a rigid body displacement from those given by Love.

4. It is convenient to introduce non-dimensional co-ordinates (ρ, ζ) defined by

$$\rho = r/h, \quad \zeta = z/h. \quad (4.1)$$

When the plate is of finite thickness $2h$ the boundary conditions to be satisfied on the faces $\zeta = \pm 1$ of the plate are*

$$\widehat{z z} = \widehat{r z} = \widehat{\theta z} = 0, \quad (4.2)$$

and the plane strain solution does not give a zero value of the normal stress $\widehat{z z}$ on the faces. It is therefore necessary to find a suitable stress system which has no singularities in the plate, and which cancels the stresses $\widehat{z z}$ on the faces $\zeta = \pm 1$ without introducing shear stresses there. The additional stress system must also vanish at infinity.

It is therefore necessary to find functions ω, ϕ which are even in the co-ordinate ζ , and are such that when $\zeta = \pm 1$

$$\left. \begin{aligned} \frac{\partial \omega}{\partial z} + \frac{\partial \phi}{\partial z} + 2z \frac{\partial^2 \phi}{\partial z^2} &= 0, \\ \frac{\partial^2 \omega}{\partial z^2} - \frac{\partial^2 \phi}{\partial z^2} + 2z \frac{\partial^3 \phi}{\partial z^3} &= \frac{P\eta \cos \theta}{4\mu\pi(1-\eta)r}. \end{aligned} \right\} \quad (4.3)$$

The first of these conditions ensures that $\widehat{r z} = \widehat{\theta z} = 0$ at $\zeta = \pm 1$, and the second condition cancels the stress $\widehat{z z}$ on these faces. Suitable forms for ω, ϕ are

$$\left. \begin{aligned} \omega &= \cos \theta \int_0^\infty f(u) J_1(u\rho) \cosh u\zeta du, \\ \phi &= \cos \theta \int_0^\infty g(u) J_1(u\rho) \cosh u\zeta du. \end{aligned} \right\} \quad (4.4)$$

The conditions (4.3) are now satisfied at $\zeta = \pm 1$ if

$$\left. \begin{aligned} f(u) \sinh u + g(u) (\sinh u + 2u \cosh u) &= 0, \\ \int_0^\infty \{f(u) \cosh u - g(u) (\cosh u - 2u \sinh u)\} u^2 J_1(u\rho) du &= \frac{P\eta h}{4\pi\mu\rho(1-\eta)}. \end{aligned} \right\} \quad (4.5)$$

The second equation of (4.5) is satisfied if

$$f(u) \cosh u - g(u) (\cosh u - 2u \sinh u) = \frac{P\eta h}{4\pi\mu u^2(1-\eta)}, \quad (4.6)$$

so that, solving for $f(u)$ and $g(u)$,

$$\left. \begin{aligned} f(u) &= \frac{P\eta h (\sinh u + 2u \cosh u)}{4\pi\mu u^2(1-\eta) \Sigma}, \\ g(u) &= -\frac{P\eta h \sinh u}{4\pi\mu u^2(1-\eta) \Sigma}, \end{aligned} \right\} \quad (4.7)$$

where

$$\Sigma = 2u + \sinh 2u. \quad (4.8)$$

* Except possibly at $\rho = 0$, $\zeta = \pm 1$

Thus the required values for ω and ϕ are

$$\left. \begin{aligned} \omega &= \frac{P\eta h \cos \theta}{4\pi\mu(1-\eta)} \int_0^\infty \frac{(\sinh u + 2u \cosh u) \cosh u \zeta J_1(u\rho)}{u^2 \Sigma} du, \\ \phi &= -\frac{P\eta h \cos \theta}{4\pi\mu(1-\eta)} \int_0^\infty \frac{\sinh u \cosh u \zeta J_1(u\rho)}{u^2 \Sigma} du. \end{aligned} \right\} \quad (4.9)$$

These integrals are not convergent at the lower limit, but the divergent terms (which represent a rigid body displacement) are trivial and may be removed by adding suitable terms which do not affect the boundary conditions (4.2). Thus satisfactory solutions for ω and ϕ , which converge at the lower limit, are

$$\left. \begin{aligned} \omega &= \frac{P\eta h \cos \theta}{4\pi\mu(1-\eta)} \int_0^\infty \left\{ \frac{(\sinh u + 2u \cosh u) \cosh u \zeta J_1(u\rho)}{u^2 \Sigma} - \frac{3\rho e^{-u}}{8u} \right\} du, \\ \phi &= -\frac{P\eta h \cos \theta}{4\pi\mu(1-\eta)} \int_0^\infty \left\{ \frac{\sinh u \cosh u \zeta J_1(u\rho)}{u^2 \Sigma} - \frac{\rho e^{-u}}{8u} \right\} du. \end{aligned} \right\} \quad (4.10)$$

5. By substituting the potential functions found above in equations (2.12), the stresses from the combined system which satisfies the boundary conditions (4.2) are found to be

$$\begin{aligned} \frac{2\pi r}{P \cos \theta} \cdot \widehat{rr} &= -\frac{3-2\eta}{2(1-\eta)} + \frac{2\eta\rho}{(1-\eta)} \int_0^\infty \left[\{(2\eta-1) \sinh u \cosh u \zeta + u \cosh u \cosh u \zeta \right. \\ &\quad \left. - u \zeta \sinh u \sinh u \zeta\} J_1''(u\rho) + 2\eta \sinh u \cosh u \zeta J_1(u\rho) \right] \Sigma^{-1} du, \end{aligned} \quad (5.1)$$

$$\begin{aligned} \frac{2\pi r}{P \cos \theta} \cdot \widehat{\theta\theta} &= \frac{1-2\eta}{2(1-\eta)} - \frac{2\eta\rho}{(1-\eta)} \int_0^\infty \left[\{(2\eta-1) \sinh u \cosh u \zeta + u \cosh u \cosh u \zeta \right. \\ &\quad \left. - u \zeta \sinh u \sinh u \zeta\} \{J_1''(u\rho) + J_1(u\rho)\} - 2\eta \sinh u \cosh u \zeta J_1(u\rho) \right] \Sigma^{-1} du, \end{aligned} \quad (5.2)$$

$$\begin{aligned} \frac{2\pi r}{P \cos \theta} \cdot \widehat{zz} &= -\frac{\eta}{(1-\eta)} + \frac{2\eta\rho}{(1-\eta)} \int_0^\infty \left\{ \sinh u \cosh u \zeta + u \cosh u \cosh u \zeta \right. \\ &\quad \left. - u \zeta \sinh u \sinh u \zeta \right\} J_1(u\rho) \Sigma^{-1} du, \end{aligned} \quad (5.3)$$

$$\frac{2\pi r}{P \sin \theta} \cdot \widehat{\theta z} = -\frac{2\eta}{(1-\eta)} \int_0^\infty \{ \cosh u \sinh u \zeta - \zeta \sinh u \cosh u \zeta \} J_1(u\rho) \Sigma^{-1} du, \quad (5.4)$$

$$\frac{2\pi r}{P \cos \theta} \cdot \widehat{rz} = \frac{2\eta\rho}{(1-\eta)} \int_0^\infty \{ u \cosh u \sinh u \zeta - u \zeta \sinh u \cosh u \zeta \} J_1'(u\rho) \Sigma^{-1} du, \quad (5.5)$$

$$\begin{aligned} \frac{2\pi r}{P \sin \theta} \cdot \widehat{r\theta} &= \frac{1-2\eta}{2(1-\eta)} + \frac{2\eta\rho}{(1-\eta)} \int_0^\infty \left\{ (2\eta-1) \sinh u \cosh u \zeta + u \cosh u \cosh u \zeta \right. \\ &\quad \left. - u \zeta \sinh u \sinh u \zeta \right\} \{J_1''(u\rho) + J_1(u\rho)\} \Sigma^{-1} du. \end{aligned} \quad (5.6)$$

It will be seen that the parts of the potential functions which were added to secure convergence make no contribution to the stresses.

6. AVERAGE VALUES OF THE STRESSES

By integrating the stresses obtained in the previous section the following *average* values are found:

$$\left. \begin{aligned} \frac{2\pi r}{P \cos \theta} \cdot \bar{r}r &= -\frac{3-2\eta}{2(1-\eta)} + \frac{\rho\eta^2}{(1-\eta)} \{G(\rho) + H(\rho)\}, \\ \frac{2\pi r}{P \cos \theta} \cdot \bar{\theta}\theta &= \frac{1-2\eta}{2(1-\eta)} + \frac{\rho\eta^2}{(1-\eta)} \{3G(\rho) - H(\rho)\}, \\ \frac{2\pi r}{P \cos \theta} \cdot \bar{z}z &= \frac{\eta}{(1-\eta)} \{4\rho G(\rho) - 1\}, \\ \frac{2\pi r}{P \sin \theta} \cdot \bar{r}\theta &= \frac{1-2\eta}{2(1-\eta)} + \frac{\rho\eta^2}{(1-\eta)} \{G(\rho) + H(\rho)\}, \end{aligned} \right\} \quad (6.1)$$

$$\text{where} \quad G(\rho) = \int_0^\infty \frac{J_1(u\rho) \sinh^2 u}{u\Sigma} du, \quad H(\rho) = \int_0^\infty \frac{J_3(u\rho) \sinh^2 u}{u\Sigma} du. \quad (6.2)$$

The values of $\bar{r}r$ and $\bar{\theta}z$ both vanish. With the help of the identity

$$\frac{\sinh^2 u}{\Sigma} = \frac{1}{2} - \frac{2u + 1 - e^{-2u}}{2\Sigma}, \quad (6.3)$$

the integrals (6.2) can be written in the form

$$\left. \begin{aligned} G(\rho) &= \frac{1}{2} \int_0^\infty \frac{J_1(u\rho)}{u} du - \frac{1}{2} \int_0^\infty \frac{(2u + 1 - e^{-2u}) J_1(u\rho)}{u\Sigma} du, \\ H(\rho) &= \frac{1}{2} \int_0^\infty \frac{J_3(u\rho)}{u} du - \frac{1}{2} \int_0^\infty \frac{(2u + 1 - e^{-2u}) J_3(u\rho)}{u\Sigma} du. \end{aligned} \right\} \quad (6.4)$$

The integrals not involving Σ can be evaluated immediately, using the results (Watson 1944, p. 391)

$$\int_0^\infty \frac{J_1(u\rho)}{u} du = 1, \quad \int_0^\infty \frac{J_3(u\rho)}{u} du = \frac{1}{3}, \quad (6.5)$$

provided $\rho > 0$. The other integrals may be evaluated by expanding the Bessel functions and integrating term by term, making use of the known integrals

$$I_s = \int_0^\infty \frac{u^s}{\Sigma} du, \quad J_s = \int_0^\infty \frac{u^s e^{-2u}}{\Sigma} du, \quad (6.6)$$

which have been tabulated by Howland* (1930). When $s > 20$ it is sufficient to take the asymptotic value of I_s which is $s!/2^s$, while the J_s integrals can be neglected compared with I_s . In addition it is necessary to know the value of $I_0 - J_0$. This has been evaluated by numerical integration and is 0.39900.

The resulting series are only convergent for $\rho \leq 2$. This range of values of ρ , however, is found to be sufficient. When ρ is small the series are rapidly convergent, but

* The values of I_{11} and I_{14} were corrected by Howland in a later paper (Howland & Stevenson 1933).

when ρ is greater than 1 the convergence is slow and the series may best be summed by using an Euler transformation, since the terms of the series alternate in sign. The values found in this way are recorded in table 1. The series for the integrals $G(\rho)$, $H(\rho)$ may be partially summed, leaving a series which is convergent for values of ρ up to 4. The numerical values in table 1 were checked by this method.

TABLE 1

ρ	0	0.2	0.4	0.6	0.8	1.0
G	0.5000	0.4420	0.3863	0.3348	0.2887	0.2487
H	0.1667	0.1665	0.1657	0.1635	0.1597	0.1544
ρ	1.2	1.4	1.6	1.8	2.0	
G	0.2149	0.1867	0.1635	0.1446	0.1291	
H	0.1478	0.1402	0.1322	0.1240	0.1159	

 TABLE 2. VALUES OF AVERAGE STRESSES FOR $\eta = 0.25$

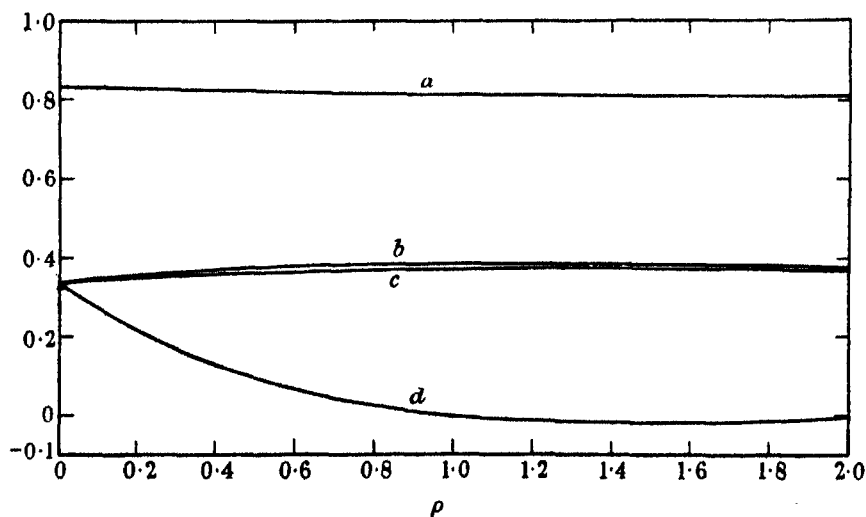
ρ	0	0.2	0.4	0.6	0.8	1.0
$\frac{2\pi r}{P \cos \theta} \bar{r}$	-1.6667	-1.6565	-1.6483	-1.6418	-1.6368	-1.6331
$\frac{2\pi r}{P \cos \theta} \bar{\theta}$	0.3333	0.3527	0.3664	0.3754	0.3804	0.3826
$\frac{2\pi r}{P \cos \theta} \bar{z}$	-0.3333	-0.2155	-0.1273	-0.0655	-0.0254	-0.0017
$\frac{2\pi r}{P \sin \theta} \bar{r}$	0.3333	0.3435	0.3517	0.3582	0.3632	0.3669
ρ	1.2	1.4	1.6	1.8	2.0	∞
$\frac{2\pi r}{P \cos \theta} \bar{r}$	-1.6304	-1.6285	-1.6272	-1.6264	-1.6258	-1.6250
$\frac{2\pi r}{P \cos \theta} \bar{\theta}$	0.3830	0.3823	0.3811	0.3798	0.3786	0.3750
$\frac{2\pi r}{P \cos \theta} \bar{z}$	0.0105	0.0152	0.0155	0.0137	0.0109	0
$\frac{2\pi r}{P \sin \theta} \bar{r}$	0.3696	0.3715	0.3728	0.3736	0.3742	0.3750

The values of the stresses were calculated from equation (6.1) for two values of Poisson's ratio $\eta = 0.25$ and $\eta = 0.5$ (corresponding to an incompressible material), and the results are recorded in tables 2 and 3. The values for $\rho = 0$ (i.e. $h \rightarrow \infty$) are those for plane strain, and for $\rho \rightarrow \infty$ (i.e. $h \rightarrow 0$) the values are those given by the theory of generalized plane stress. The results are shown graphically in figures* 1 and 2. Although the stresses are not found for values of ρ between 2 and ∞ it appears probable that little variation will occur in this range of values of ρ .

* For convenience, in figures 1 to 6, the radial stress $\bar{r}$ is halved in magnitude before plotting.

TABLE 3. VALUES OF AVERAGE STRESSES FOR $\eta = 0.5$

ρ	0	0.2	0.4	0.6	0.8	1.0
$\frac{2\pi r \cdot \tilde{r}\tilde{r}}{P \cos \theta}$	-2.0	-1.9392	-1.8896	-1.8505	-1.8206	-1.7984
$\frac{2\pi r \cdot \tilde{\theta}\tilde{\theta}}{P \cos \theta}$	0	0.1160	0.1986	0.2523	0.2826	0.2959
$\frac{2\pi r \cdot \tilde{z}\tilde{z}}{P \cos \theta}$	-1.0000	-0.6464	-0.3819	-0.1965	-0.0762	-0.0052
$\frac{2\pi r \cdot \tilde{r}\tilde{\theta}}{P \sin \theta}$	0	0.06085	0.1104	0.1495	0.1794	0.2016
ρ	1.2	1.4	1.6	1.8	2.0	∞
$\frac{2\pi r \cdot \tilde{r}\tilde{r}}{P \cos \theta}$	-1.7824	-1.7712	-1.7634	-1.7583	-1.7550	-1.7500
$\frac{2\pi r \cdot \tilde{\theta}\tilde{\theta}}{P \cos \theta}$	0.2981	0.2939	0.2866	0.2788	0.2714	0.2500
$\frac{2\pi r \cdot \tilde{z}\tilde{z}}{P \cos \theta}$	0.0315	0.0455	0.0464	0.0411	0.0328	0
$\frac{2\pi r \cdot \tilde{r}\tilde{\theta}}{P \sin \theta}$	0.2176	0.2288	0.2366	0.2417	0.2450	0.2500

FIGURE 1. Average stresses when $\eta = 0.25$.

Curve a	$-\frac{2\pi r \cdot \tilde{r}\tilde{r}}{P \cos \theta} \frac{1}{2}$	Curve c	$\frac{2\pi r \cdot \tilde{r}\tilde{\theta}}{P \sin \theta}$
Curve b	$\frac{2\pi r \cdot \tilde{\theta}\tilde{\theta}}{P \cos \theta}$	Curve d	$-\frac{2\pi r \cdot \tilde{z}\tilde{z}}{P \cos \theta}$

When Poisson's ratio is 0.25 it is seen that the generalized plane-stress value for $\bar{r}\bar{r}/\cos\theta$ (i.e. corresponding to $\rho \rightarrow \infty$) is a very good approximation to the actual average value of this component of stress over a wide range of values of ρ , the greatest difference being only about $2\frac{1}{2}\%$ when the plate is very wide ($\rho \rightarrow 0$). There is a greater percentage variation in the values of $\bar{\theta}\bar{\theta}/\cos\theta$ and $\bar{r}\bar{\theta}/\sin\theta$, particularly for small values of ρ . The average stress $\bar{z}\bar{z}$, which is neglected in one form of the generalized plane-stress theory, is very small over a wide range of values of ρ , but when ρ is smaller than about 0.4, $\bar{z}\bar{z}$ becomes comparable with $\bar{\theta}\bar{\theta}$ and cannot be ignored. The small values of ρ , however, correspond either to wide plates, for which the plane-strain solution is more applicable, or for points fairly near the applied force where the mathematical solution is of doubtful physical value.

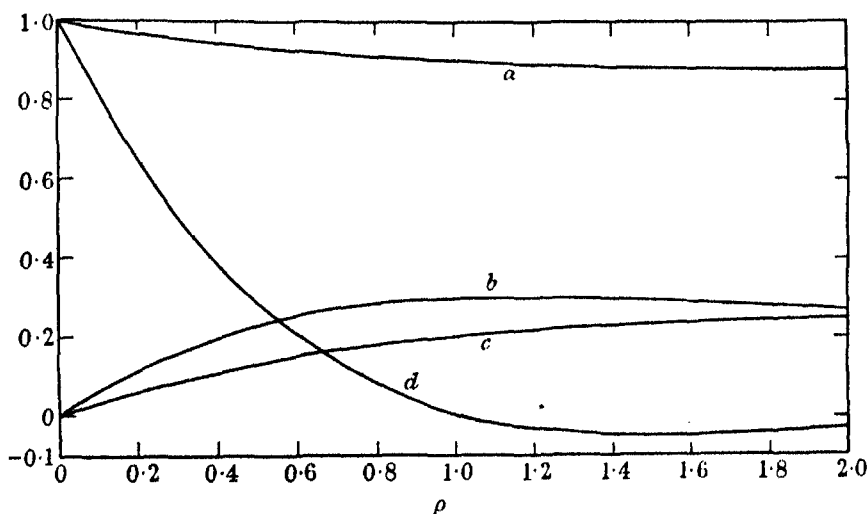


FIGURE 2. Average stresses when $\eta = 0.5$.

Curve a $-\frac{2\pi r}{P \cos \theta} \frac{\bar{r}\bar{r}}{2}$	Curve c $\frac{2\pi r}{P \sin \theta} \bar{r}\bar{\theta}$
Curve b $\frac{2\pi r}{P \cos \theta} \bar{\theta}\bar{\theta}$	Curve d $-\frac{2\pi r}{P \cos \theta} \bar{z}\bar{z}$

When Poisson's ratio has the limiting value 0.5 for an incompressible material there is much greater variation from the generalized plane stress average values of the stresses, particularly when ρ is less than 1, the greatest variations occurring in $\bar{\theta}\bar{\theta}/\cos\theta$ and $\bar{r}\bar{\theta}/\sin\theta$. The average stress $\bar{z}\bar{z}$ is still small for a wide range of values of ρ , but when ρ is less than about 0.8 its value is comparable in magnitude with the other stresses.

Broadly speaking it may be concluded that the generalized plane-stress theory gives quite a good approximation for the values of the average stress $\bar{r}\bar{r}$ for moderate values of Poisson's ratio η , the approximation decreasing a little in accuracy as η

approaches the limiting value 0.5. The generalized plane-stress theory is a little less reliable in its estimate of the remaining average stresses, particularly for the larger values of η .

Attention in the next sections is directed to the actual values of the stresses at particular points of the plate in order to get some idea of the variation from the average values.

7. VALUES OF THE STRESSES ON THE SURFACE OF THE PLATE

The values of the stresses on the surface of the plate may be obtained by writing $\zeta = \pm 1$ in the formulae of § 5. After some reduction it is found that*

$$\left. \begin{aligned} \frac{2\pi r \cdot \bar{r}}{P \cos \theta} &= \frac{2\eta^2 + 3\eta - 3}{2(1-\eta)} + \frac{\eta}{1-\eta} \{-(3+\eta)L(\rho) + (1-\eta)M(\rho)\}, \\ \frac{2\pi r \cdot \bar{\theta}}{P \cos \theta} &= \frac{2\eta^2 - \eta + 1}{2(1-\eta)} - \frac{\eta}{1-\eta} \{(1+3\eta)L(\rho) + (1-\eta)M(\rho)\}, \\ \frac{2\pi r \cdot \bar{r}\theta}{P \sin \theta} &= \frac{1-2\eta}{2} + \eta\{L(\rho) + M(\rho)\}, \end{aligned} \right\} \quad (7.1)$$

$$\text{where} \quad L(\rho) = \int_0^\infty \frac{u\rho J_1(u\rho)}{\Sigma} du, \quad M(\rho) = \int_0^\infty \frac{u\rho J_3(u\rho)}{\Sigma} du. \quad (7.2)$$

TABLE 4

ρ	0	0.2	0.4	0.6	0.8	1.0
L	0	0.007548	0.02870	0.05955	0.09506	0.1305
M	0	0.0000433	0.000653	0.003002	0.008348	0.01745
ρ	1.2	1.4	1.6	1.8	2.0	∞
L	0.1626	0.1892	0.2098	0.2249	0.2351	0.2500
M	0.03032	0.04629	0.06429	0.08320	0.1020	0.2500

TABLE 5. VALUES OF THE STRESSES ON THE SURFACE OF THE PLATE FOR $\eta = 0.25$

ρ	0	0.2	0.4	0.6	0.8	1.0
$\frac{2\pi r \cdot \bar{r}}{P \cos \theta}$	-1.4167	-1.4248	-1.4476	-1.4804	-1.5176	-1.5537
$\frac{2\pi r \cdot \bar{\theta}}{P \cos \theta}$	0.5833	0.5789	0.5664	0.5478	0.5258	0.5028
$\frac{2\pi r \cdot \bar{r}\theta}{P \sin \theta}$	0.2500	0.2519	0.2573	0.2656	0.2759	0.2870
ρ	1.2	1.4	1.6	1.8	2.0	∞
$\frac{2\pi r \cdot \bar{r}}{P \cos \theta}$	-1.5852	-1.6100	-1.6279	-1.6395	-1.6459	-1.6250
$\frac{2\pi r \cdot \bar{\theta}}{P \cos \theta}$	0.4809	0.4614	0.4449	0.4313	0.4207	0.3750
$\frac{2\pi r \cdot \bar{r}\theta}{P \sin \theta}$	0.2982	0.3089	0.3185	0.3270	0.3343	0.3750

* Except when $\rho = 0$.

The stresses $\hat{z}\hat{z}$, $\hat{\theta}\hat{z}$ and $\hat{r}\hat{z}$ vanish on the surface of the plate. For values of ρ from 0 to 2 the integrals $L(\rho)$, $M(\rho)$ may be evaluated by a similar method to that used for the integrals $G(\rho)$, $H(\rho)$ in § 6. The numerical values are given in table 4. Using these values the surface stresses (7.1) were calculated for values of η equal to 0.25 and 0.5,

TABLE 6. VALUES OF THE STRESSES ON THE SURFACE OF THE PLATE FOR $\eta = 0.5$

ρ	0	0.2	0.4	0.6	0.8	1.0
$\frac{2\pi r \cdot \hat{r}\hat{r}}{P \cos \theta}$	-1.0000	-1.0264	-1.1001	-1.2069	-1.3285	-1.4480
$\frac{2\pi r \cdot \hat{\theta}\hat{\theta}}{P \cos \theta}$	1.0000	0.9811	0.9279	0.8496	0.7582	0.6650
$\frac{2\pi r \cdot \hat{r}\hat{\theta}}{P \sin \theta}$	0	0.0038	0.0147	0.0313	0.0517	0.0740
ρ	1.2	1.4	1.6	1.8	2.0	∞
$\frac{2\pi r \cdot \hat{r}\hat{r}}{P \cos \theta}$	-1.5539	-1.6391	-1.7022	-1.7456	-1.7719	-1.7500
$\frac{2\pi r \cdot \hat{\theta}\hat{\theta}}{P \cos \theta}$	0.5783	0.5039	0.4434	0.3962	0.3613	0.2500
$\frac{2\pi r \cdot \hat{r}\hat{\theta}}{P \sin \theta}$	0.0965	0.1177	0.1370	0.1541	0.1686	0.2500

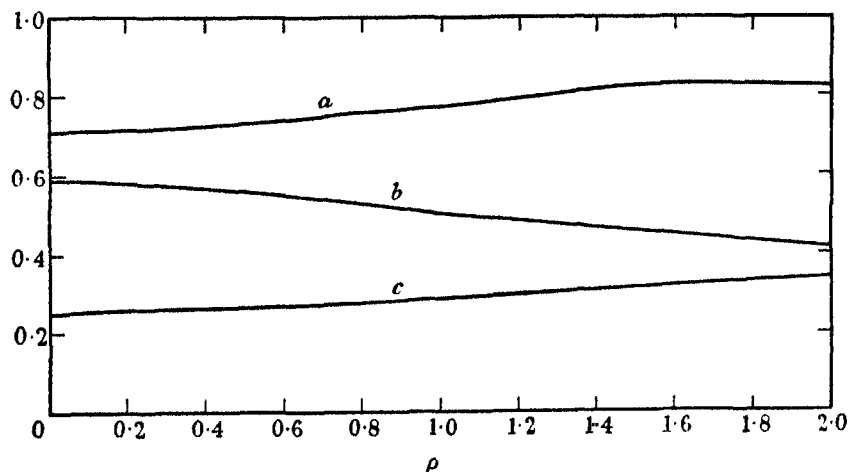


FIGURE 3. Values of stresses at the faces of the plate when $\eta = 0.25$.

$$\text{Curve } a = -\frac{2\pi r \cdot \hat{r}\hat{r}}{P \cos \theta}, \quad \text{Curve } b = \frac{2\pi r \cdot \hat{\theta}\hat{\theta}}{P \cos \theta}, \quad \text{Curve } c = \frac{2\pi r \cdot \hat{r}\hat{\theta}}{P \sin \theta}.$$

and the results are recorded in tables 5 and 6. These results are shown graphically in figures 3 and 4. The stresses are also compared with their average values in figures 7 to 12. It should be noticed that the values given in tables 5 and 6 for $\rho \rightarrow 0$ are different from the plane strain values which correspond to $\rho = 0$ owing to the removal of the surface stress $\hat{z}\hat{z}$ in the present solution.

Near $\rho \approx 2$, and possibly for $\rho > 2$, the stress $\widehat{rr}$ at the surface of the plate is very slightly in excess of the average value. For smaller values of ρ , $\widehat{rr}$ is very much smaller than the average values especially for the larger values of η . The shear stress $\widehat{r\theta}$ at the surface always appears to be smaller than the average value, the greatest differences again occurring for the larger values of η . The values of $\widehat{\theta\theta}$ at the surface are considerably in excess of the average values for the range of ρ considered here, especially for large values of η .

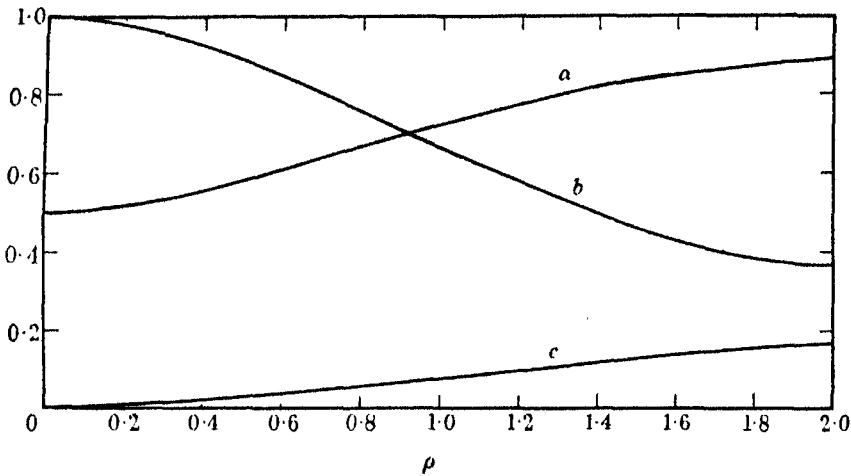


FIGURE 4. Values of stresses at the faces of the plate when $\eta = 0.5$.

$$\text{Curve } a \quad - \frac{2\pi r}{P \cos \theta} \widehat{rr}, \quad \text{Curve } b \quad \frac{2\pi r}{P \cos \theta} \widehat{\theta\theta}, \quad \text{Curve } c \quad \frac{2\pi r}{P \sin \theta} \widehat{r\theta}.$$

8. VALUES OF THE STRESSES AT POINTS INSIDE THE PLATE

For internal points the stresses (5.1) to (5.6) may conveniently be expressed in the forms

$$\begin{aligned} \frac{2\pi r}{P \cos \theta} \widehat{rr} = & -\frac{3-2\eta}{2(1-\eta)} + \frac{\eta\rho}{4(1-\eta)} \\ & \times [(3+2\eta)\{I_2(1+\zeta) + I_3(1-\zeta)\} - 3(1-\zeta)I_3(1+\zeta) - 3(1+\zeta)I_3(1-\zeta) \\ & + (2\eta-1)\{I_4(1+\zeta) + I_4(1-\zeta)\} + (1-\zeta)I_5(1+\zeta) + (1+\zeta)I_5(1-\zeta)], \end{aligned} \quad (8.1)$$

$$\begin{aligned} \frac{2\pi r}{P \cos \theta} \widehat{\theta\theta} = & \frac{1-2\eta}{2(1-\eta)} + \frac{\eta\rho}{4(1-\eta)} \\ & \times [(\theta\eta+1)\{I_2(1+\zeta) + I_3(1-\zeta)\} - (1-\zeta)I_3(1+\zeta) - (1+\zeta)I_3(1-\zeta) \\ & - (2\eta-1)\{I_4(1+\zeta) + I_4(1-\zeta)\} - (1-\zeta)I_5(1+\zeta) - (1+\zeta)I_5(1-\zeta)], \end{aligned} \quad (8.2)$$

$$\frac{2\pi r}{P \cos \theta} \widehat{r\theta} = -\frac{\eta}{1-\eta} + \frac{\eta\rho}{(1-\eta)} \{I_2(1+\zeta) + I_2(1-\zeta) + (1-\zeta)I_3(1+\zeta) + (1+\zeta)I_3(1-\zeta)\}, \quad (8.3)$$

$$\frac{2\pi r \cdot \partial z}{P \sin \theta} = -\frac{\eta}{(1-\eta)} \{ (1-\zeta) I_2(1+\zeta) - (1+\zeta) I_2(1-\zeta) \}, \quad (8.4)$$

$$\frac{2\pi r \cdot \partial r}{P \cos \theta} = \frac{\eta}{1-\eta} \{ (1-\zeta) I_1(1+\zeta) - (1+\zeta) I_1(1-\zeta) - (1-\zeta) I_2(1+\zeta) + (1+\zeta) I_2(1-\zeta) \}, \quad (8.5)$$

$$\begin{aligned} \frac{2\pi r \cdot \partial \theta}{P \sin \theta} = & \frac{1-2\eta}{2(1-\eta)} + \frac{\eta \rho}{4(1-\eta)} \\ & \times [(2\eta-1) \{ I_2(1+\zeta) + I_2(1-\zeta) \} + (1-\zeta) I_3(1+\zeta) + (1+\zeta) I_3(1-\zeta) \\ & + (2\eta-1) \{ I_4(1+\zeta) + I_4(1-\zeta) \} + (1-\zeta) I_5(1+\zeta) + (1+\zeta) I_5(1-\zeta)], \end{aligned} \quad (8.6)$$

$$\text{where*} \quad \left. \begin{aligned} I_1(x) &= \int_0^\infty \frac{u \rho \sinh ux J_0(u\rho)}{\Sigma} du, & I_2(x) &= \int_0^\infty \frac{\sinh ux J_1(u\rho)}{\Sigma} du, \\ I_3(x) &= \int_0^\infty \frac{u \cosh ux J_1(u\rho)}{\Sigma} du, & I_4(x) &= \int_0^\infty \frac{\sinh ux J_3(u\rho)}{\Sigma} du, \\ I_5(x) &= \int_0^\infty \frac{u \cosh ux J_3(u\rho)}{\Sigma} du. \end{aligned} \right\} \quad (8.7)$$

It is not possible to evaluate these integrals by the methods used in the previous sections owing to the absence of tabulated values of $\int_0^\infty \frac{u^s e^{-tu}}{\Sigma} du$ for values of t other than 0 and 2.

Sneddon (1946) has used an approximate expression for Σ in evaluating similar types of integrals to these found here (the first three integrals in (8.7) appear in Sneddon's paper), and this approximation is probably sufficiently accurate for the present work. Sneddon replaces $f(u) = u/(u + \sinh u)$ by

$$f_1(u) = (\beta u + \frac{1}{2}) e^{-\nu u} + 2ue^{-u},$$

where β and ν are chosen so that the area under the curve $f_1 - f$ is as small as possible. This condition is said by Sneddon to be satisfied to a large degree when $\beta = -1.55$, $\nu = 1.40$.

Using this approximation the integrals (8.7) can be written

$$\left. \begin{aligned} I_1(x) &= F_1(2-x) - F_1(2+x) + \frac{1}{2}\beta \{ F_1(2\nu-x) - F_1(2\nu+x) \} + \frac{1}{8} \{ F_2(2\nu-x) - F_2(2\nu+x) \}, \\ I_2(x) &= F_2(2-x) - F_2(2+x) + \frac{1}{2}\beta \{ F_2(2\nu-x) - F_2(2\nu+x) \} + \frac{1}{8} \{ F_3(2\nu-x) - F_3(2\nu+x) \}, \\ I_3(x) &= F_3(2-x) + F_3(2+x) + \frac{1}{2}\beta \{ F_3(2\nu-x) + F_3(2\nu+x) \} + \frac{1}{8} \{ F_4(2\nu-x) + F_4(2\nu+x) \}, \\ I_4(x) &= F_4(2-x) - F_4(2+x) + \frac{1}{2}\beta \{ F_4(2\nu-x) - F_4(2\nu+x) \} + \frac{1}{8} \{ F_5(2\nu-x) - F_5(2\nu+x) \}, \\ I_5(x) &= F_5(2-x) + F_5(2+x) + \frac{1}{2}\beta \{ F_5(2\nu-x) + F_5(2\nu+x) \} + \frac{1}{8} \{ F_6(2\nu-x) + F_6(2\nu+x) \}, \end{aligned} \right\} \quad (8.8)$$

* These integrals must not be confused with the I_s integrals in (6.6) or with Bessel's functions of imaginary argument.

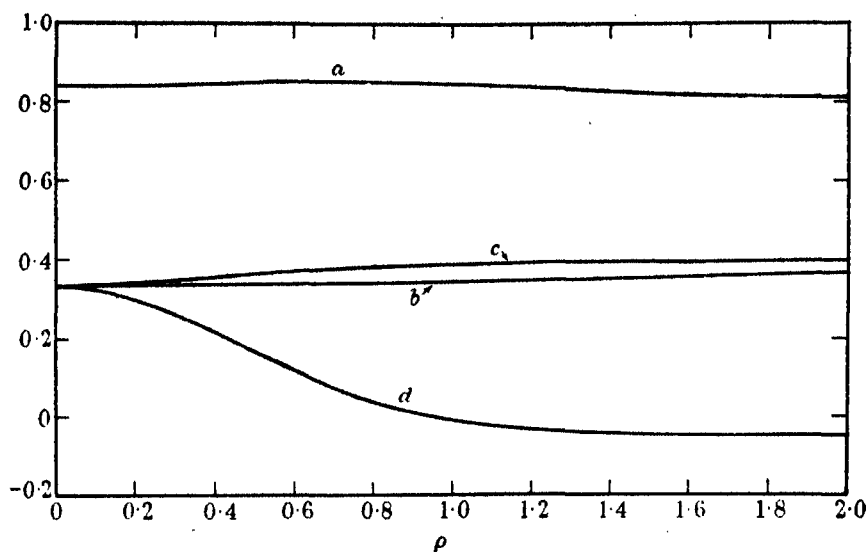
where

$$\left. \begin{aligned} F_1(x) &= \int_0^\infty \rho u e^{-xu} J_0(u\rho) du = \frac{\rho x}{(x^2 + \rho^2)^{\frac{1}{2}}}, \\ F_2(x) &= \int_0^\infty \rho e^{-xu} J_0(u\rho) du = \frac{\rho}{(x^2 + \rho^2)^{\frac{1}{2}}}, \\ F_3(x) &= \int_0^\infty e^{-xu} J_1(u\rho) du = \frac{\rho}{(x^2 + \rho^2)^{\frac{1}{2}} \{(x^2 + \rho^2)^{\frac{1}{2}} + x\}}, \\ F_4(x) &= \int_0^\infty u^{-1} e^{-xu} J_1(u\rho) du = \frac{\rho}{(x^2 + \rho^2)^{\frac{1}{2}} + x}, \\ F_5(x) &= \int_0^\infty u e^{-xu} J_1(u\rho) du = \frac{\rho}{(x^2 + \rho^2)^{\frac{1}{2}}}, \\ F_6(x) &= \int_0^\infty e^{-xu} J_3(u\rho) du = \frac{\rho^3}{(x^2 + \rho^2)^{\frac{1}{2}} \{(x^2 + \rho^2)^{\frac{1}{2}} + x\}^3}, \\ F_7(x) &= \int_0^\infty u^{-1} e^{-xu} J_3(u\rho) du = \frac{\rho^3}{3 \{(x^2 + \rho^2)^{\frac{1}{2}} + x\}^3}, \\ F_8(x) &= \int_0^\infty u e^{-xu} J_3(u\rho) du = \frac{\rho^3 \{3(x^2 + \rho^2)^{\frac{1}{2}} + x\}}{(x^2 + \rho^2)^{\frac{1}{2}} \{(x^2 + \rho^2)^{\frac{1}{2}} + x\}^3} \end{aligned} \right\} \quad (8.9)$$

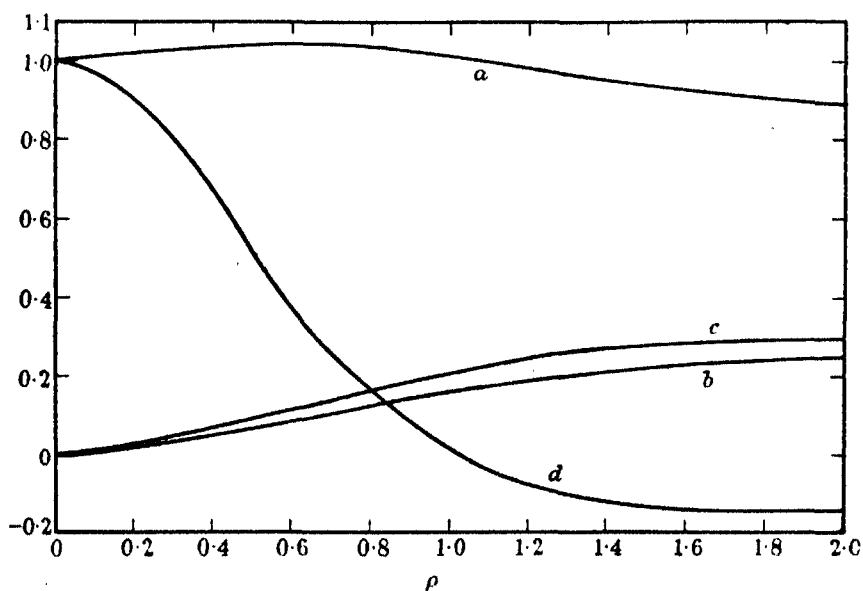
for suitable values of ρ and x . Using these formulae the stresses may be obtained at any point inside the plate. Values of the stresses on the middle plane $\zeta = 0$ are likely to be of particular interest and calculations here have been confined to these stresses. The stresses for $\zeta = 0$ only depend on the integrals $I_2(1), \dots, I_5(1)$, and the values of these integrals found from (8.8) and (8.9) are shown in table 7. Using these values the stresses were then found from (8.1) to (8.6) for Poisson's ratio $\eta = 0.25$ and $\eta = 0.5$ and for values of ρ between 0 and 2. These values are recorded in tables 8 and 9 and are shown graphically in figures 5 and 6. The stresses are also compared with the average stresses and with the values at the faces of the plate in figures 7 to 12. Although the stresses in tables 8 and 9 are given to four decimal places it must be remembered that these values are obtained by using an approximation, and they may only be accurate to three or possibly two decimal places.

In general, the differences between the stresses on the middle plane and the average stresses are somewhat smaller than the differences between the face stresses and the average stresses. The stresses on the faces and on the middle plane are mainly situated numerically on opposite sides of the average values, except for some of the values of $\bar{r}\bar{\theta}$ at the smaller values of ρ and some values of $\bar{r}\bar{\tau}$ at the larger values of ρ . The values of $\bar{z}\bar{z}$ on the middle plane are mostly larger than the average values $\bar{z}\bar{z}$.

Actual values of the stresses have only been found at the middle plane and at the faces of the plate, but these values are sufficient to show that the stress distribution through the plate differs significantly in some cases from the average values especially for the larger values of η . The generalized plane-stress theory, however, appears


 FIGURE 5. Values of stresses at the middle plane when $\eta = 0.25$.

Curve a	$-\frac{2\pi r}{P \cos \theta} \frac{\widehat{r}}{2}$	Curve c	$\frac{2\pi r}{P \sin \theta} \frac{\widehat{r}\theta}{2}$
Curve b	$\frac{2\pi r}{P \cos \theta} \frac{\widehat{\theta}}{2}$	Curve d	$-\frac{2\pi r}{P \cos \theta} \frac{\widehat{z}}{2}$


 FIGURE 6. Values of stresses at the middle plane when $\eta = 0.5$.

Curve a	$-\frac{2\pi r}{P \cos \theta} \frac{\widehat{r}}{2}$	Curve c	$\frac{2\pi r}{P \sin \theta} \frac{\widehat{r}\theta}{2}$
Curve b	$\frac{2\pi r}{P \cos \theta} \frac{\widehat{\theta}}{2}$	Curve d	$-\frac{2\pi r}{P \cos \theta} \frac{\widehat{z}}{2}$

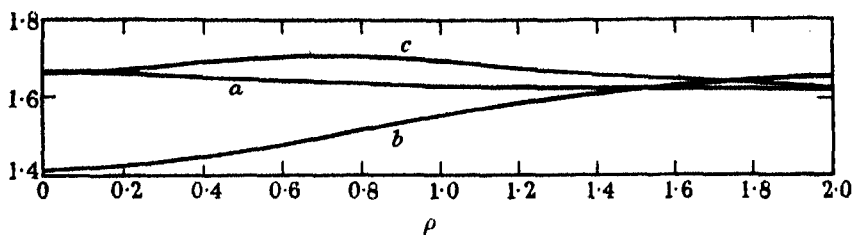


FIGURE 7. Values of $-\frac{2\pi r.\bar{r}r}{P \cos \theta}$ for $\eta = 0.25$.

Curve *a* Average values. Curve *b* Face values. Curve *c* Values on middle plane.

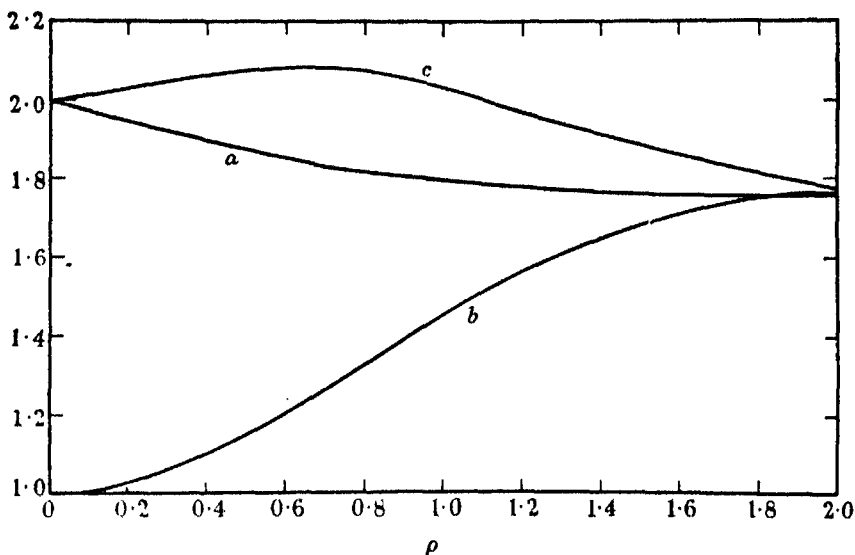


FIGURE 8. Values of $-\frac{2\pi r.\bar{r}r}{P \cos \theta}$ for $\eta = 0.5$.

Curve *a* Average values. Curve *b* Face values. Curve *c* Values on middle plane.

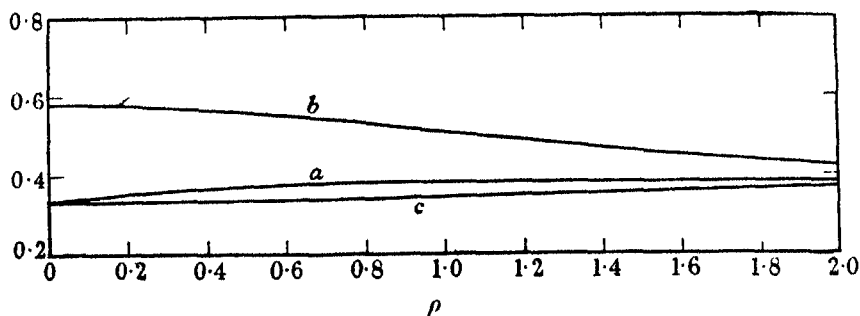


FIGURE 9. Values of $\frac{2\pi r.\bar{\theta}\theta}{P \cos \theta}$ for $\eta = 0.25$.

Curve *a* Average values. Curve *b* Face values. Curve *c* Values on middle plane.

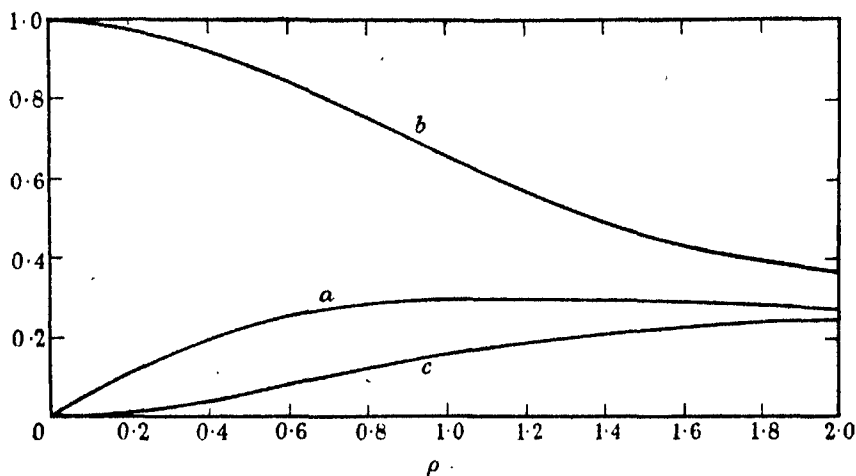


FIGURE 10. Values of $\frac{2\pi r \cdot \partial\theta}{P \cos \theta}$ for $\eta = 0.5$.

Curve *a* Average values. Curve *b* Face values. Curve *c* Values on middle plane.

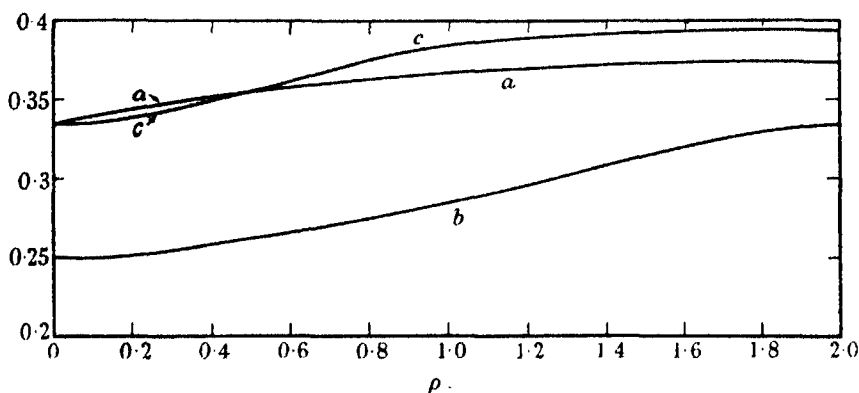


FIGURE 11. Values of $\frac{2\pi r \cdot r\theta}{P \sin \theta}$ for $\eta = 0.25$.

Curve *a* Average values. Curve *b* Face values. Curve *c* Values on middle plane.

to give a reasonable approximation for the average stresses for cases in which the theory is usually assumed to be valid, the accuracy decreasing with increase in Poisson's ratio η .

TABLE 7

ρ	0.2	0.4	0.8	1.2	1.6	2.0
$I_3(1)$	0.071314	0.12855	0.18250	0.18033	0.15811	0.13352
$I_2(1)$	0.17171	0.28875	0.33275	0.26619	0.19830	0.15030
$I_4(1)$	0.00087707	0.0060575	0.029796	0.055341	0.071451	0.078206
$I_5(1)$	0.0035804	0.023181	0.093374	0.13938	0.14818	0.13832

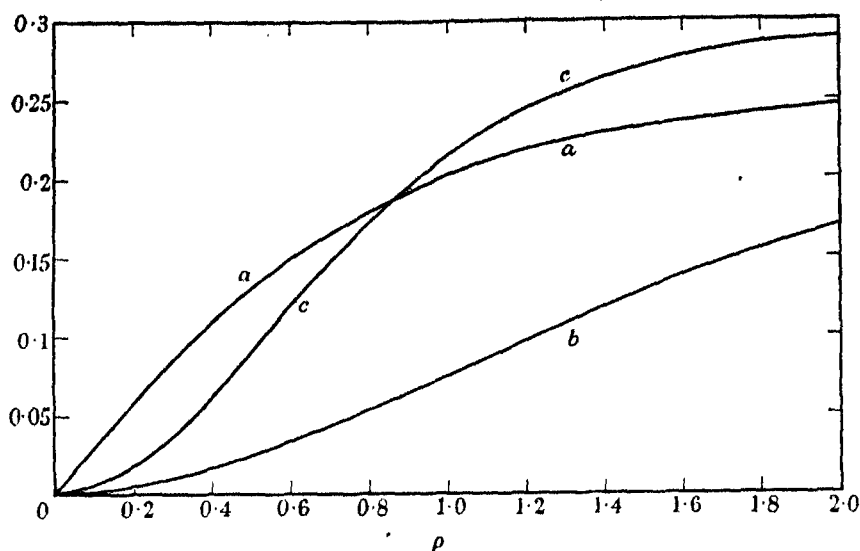


FIGURE 12. Values of $\frac{2\pi r.r\theta}{P \sin \theta}$ for $\eta = 0.5$.

Curve *a* Average values. Curve *b* Face values. Curve *c* Values on middle plane.

TABLE 8. VALUES OF THE STRESSES IN THE MIDDLE
PLANE OF THE PLATE FOR $\eta = 0.25$

ρ	0	0.2	0.4	0.8	1.2	1.6	2.0	∞
$\frac{2\pi r.r}{P \cos \theta}$	-1.6667	-1.6754	-1.6931	-1.7041	-1.6778	-1.6477	-1.6281	-1.6250
$\frac{2\pi r.\theta\theta}{P \cos \theta}$	0.3333	0.3334	0.3342	0.3393	0.3479	0.3559	0.3614	0.3750
$\frac{2\pi r.zz}{P \cos \theta}$	-0.3333	-0.3009	-0.2221	-0.0585	-0.0239	-0.0468	-0.0451	0
$\frac{2\pi r.r\theta}{P \sin \theta}$	0.3333	0.3380	0.3496	0.3760	0.3909	0.3951	0.3943	0.3750

TABLE 9. VALUES OF THE STRESSES IN THE MIDDLE
PLANE OF THE PLATE FOR $\eta = 0.5$

ρ	0	0.2	0.4	0.8	1.2	1.6	2.0	∞
$\frac{2\pi r.r}{P \cos \theta}$	-2.0000	-2.0226	-2.0658	-2.0700	-1.9627	-1.8514	-1.7785	-1.750
$\frac{2\pi r.\theta\theta}{P \cos \theta}$	0	0.0110	0.0405	0.1216	0.1895	0.2288	0.2455	0.2500
$\frac{2\pi r.zz}{P \cos \theta}$	-1.0000	-0.9028	-0.6662	-0.1756	0.0716	0.1405	0.1353	0
$\frac{2\pi r.r\theta}{P \sin \theta}$	0	0.0175	0.0624	0.1704	0.2433	0.2772	0.2886	0.2500

The paper is concluded by adding the solution of the isolated force problem for a plate of semi-infinite thickness.

9. SOLUTION FOR A PLATE OF SEMI-INFINITE THICKNESS

Consider now an isolated force of intensity P per unit length, directed along the axis of x , and situated along the z -axis from $z = 0$ to $z = \infty$, acting in a plate which is bounded by the single plane $z = 0$. The boundary conditions (4.3) are now to be satisfied when $z = 0$ and the additional stresses must vanish at $z = \infty$ as well as $r = \infty$. Suitable forms for the ω and ϕ functions are therefore

$$\omega = \cos \theta \int_0^\infty f(u) J_1(ur) e^{-uz} du, \quad \phi = \cos \theta \int_0^\infty g(u) J_1(ur) e^{-uz} du. \quad (9.1)$$

It follows from (4.3) that $f(u) + g(u) = 0$,

$$\left. \int_0^\infty \{f(u) - g(u)\} u^2 J_1(ur) du = \frac{P\eta}{4\pi\mu(1-\eta)r} \right\} \quad (9.2)$$

Solving for $f(u)$ and $g(u)$ and adding suitable terms to secure convergence of the integrals at the lower limit it is found that

$$\omega = -\phi = \frac{P\eta \cos \theta}{8\pi\mu(1-\eta)} \int_0^\infty \left\{ \frac{e^{-uz} J_1(ur)}{u^2} - \frac{re^{-u}}{2u} \right\} du. \quad (9.3)$$

From (2.12), (3.2) and (9.3) the complete stress system which satisfies the boundary condition (4.2) at the plane $z = 0$ is found to be

$$\frac{2\pi r \cdot \hat{r}r}{P \cos \theta} = \frac{2\eta - 3}{2(1-\eta)} + \frac{\eta r}{4(1-\eta)} \{ (2\eta + 3) F_3(z) - 3zF_5'(z) - (1 - 2\eta) F_6(z) + zF_8(z) \}, \quad (9.4)$$

$$\frac{2\pi r \cdot \hat{\theta}\theta}{P \cos \theta} = \frac{1 - 2\eta}{2(1-\eta)} + \frac{\eta r}{4(1-\eta)} \{ (6\eta + 1) F_3(z) - zF_5'(z) + (1 - 2\eta) F_6(z) - zF_8(z) \}, \quad (9.5)$$

$$\frac{2\pi r \cdot \hat{z}z}{P \cos \theta} = -\frac{\eta}{1-\eta} \{ 1 - rF_3(z) - rzF_5'(z) \}, \quad (9.6)$$

$$\frac{2\pi r \cdot \hat{\theta}z}{P \sin \theta} = \frac{\eta z F_3'(z)}{1-\eta}, \quad (9.7)$$

$$\frac{2\pi r \cdot \hat{z}r}{P \cos \theta} = \frac{\eta z \{ F_3(z) - F_1(z) \}}{1-\eta}, \quad (9.8)$$

$$\frac{2\pi r \cdot \hat{r}\theta}{P \sin \theta} = \frac{1 - 2\eta}{2(1-\eta)} + \frac{\eta r}{4(1-\eta)} \{ (2\eta - 1) F_3(z) + zF_5'(z) + (2\eta - 1) F_6(z) + zF_8(z) \}, \quad (9.9)$$

where $F_1(z) \dots$ are the functions defined by the equation (8.9) except that ρ in (8.9) must be replaced by r . The values of the stresses at the face $z = 0$ reduce to the simple forms

$$\frac{2\pi r \cdot \hat{r}r}{P \cos \theta} = \frac{2\eta^2 + 3\eta - 3}{2(1-\eta)}, \quad \frac{2\pi r \cdot \hat{\theta}\theta}{P \cos \theta} = \frac{2\eta^2 - \eta + 1}{2(1-\eta)}, \quad \frac{2\pi r \cdot \hat{r}\theta}{P \sin \theta} = \frac{1 - 2\eta}{2}, \quad (9.10)$$

with the remaining stresses zero. These values agree with those found in § 7 at the surfaces of the plate when $\rho \rightarrow 0$.

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On the interpretation of the Foucault test

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The diffraction theory of the Foucault test is applied to discuss the intrinsic errors of the test when the Foucault shadows are interpreted by means of the 'grazing light' fiction in the usual manner. In § 2, formulae are obtained for the effects on the Foucault shadows of an arbitrary small change in the figure of the mirror under test. In § 3 the case of a weak, narrow local zone on an otherwise nearly true mirror is discussed and expressions are obtained in terms of the zone-profile for the changes in the Foucault shadows caused by the presence of the zone. The relationship between the zone-profile inferred by means of the 'grazing light' interpretation of the shadows and that actually present on the mirror is analyzed in § 4, and it is shown that the analysis suggests some modifications in the practical technique of figuring mirrors under the Foucault test. Lastly, the general formulae established for weak, narrow zonal errors are compared with the results of computation in four selected special cases and it is shown that they may be expected to remain useful approximations in cases of interest to the practical mirror-maker.

1. INTRODUCTION

In his account of the knife-edge testing of astronomical mirrors, published in 1859, Foucault gave a simple explanation of the properties of the test in terms of ray theory. His explanation, too well known to need repeating here, leaves certain rather conspicuous appearances unexplained; nevertheless, it has served ever since as the basis of the interpretation of the test by optical workers. In the practical use of the test, the unexplained appearances, such as the brilliant line of light seen round the rim of a nearly true mirror, or the dark fringes which form on the bright slopes of a zonal error several wave-lengths deep, are ordinarily set aside as 'due to diffraction' and ignored as far as possible, while the interpretation of the knife-edge shadows is made in a semi-intuitive manner by means of the 'grazing light' fiction.

This device consists in replacing the mirror surface in imagination by a flat disk on which parallel light falls, at nearly grazing incidence, from the side opposite to the knife-edge. The Foucault shadows are interpreted as relief-shadows and the

bas-relief figure thus 'seen' on the disk is taken to represent the error-figure of the mirror. Provided that the error-slopes are sufficiently small, the error-figure inferred in this way agrees in shape with that which would be obtained by a photometric analysis of the Foucault shadows on the basis of ray theory. This does not mean, however, that it necessarily agrees in shape with the error-figure actually present on the mirror, and the relationship between the inferred and the actual errors remains a matter for investigation.

In the present paper, the diffraction theory of the test is applied to make such an investigation in the case of a weak, narrow zone on the surface of an otherwise nearly true mirror, Foucault tested with a light-source of negligible dimensions.

This case is a favourable one for discussion, since it is one in which the conclusions are not much affected by the simplifying assumption that the pinhole-size is negligible, and is not unlike cases actually met with in the zonal figuring of large astronomical mirrors.

2. EFFECT ON THE FOUCAULT SHADOWS OF A SMALL CHANGE IN FIGURE

Formulae will first be derived for the effect of an arbitrary small change in the figure of an unfinished mirror on the intensities seen under the Foucault test. The waves leaving the mirror can be described, as in a previous paper (Linfoot 1946), by means of the wave-function

$$\begin{aligned} E_1(x, y) &= e^{2\pi i \phi(x, y)} \quad (x^2 + y^2 \leq 1) \\ &= 0 \quad (x^2 + y^2 > 1), \end{aligned} \quad (2.1)$$

where $\phi(x, y)$ measures, in reflexion-fringes, the deviation of the mirror surface from the reference-sphere M_0 . The deviation may amount to many wave-lengths, but the figure of the mirror is supposed to be smooth enough to send all the reflected rays through the central parts of the aperture of the viewing system. The intensity seen under the Foucault test with the knife-edge in the plane through the centre of curvature of M_0 , but displaced laterally through a distance c from the central setting, is (Linfoot 1946, p. 83)

$$I_1(x, y; c') = |2\pi D(x, y; c')|^2, \quad (2.2)$$

where, for $-1 \leq y \leq 1$,

$$2\pi D_1(x, y; c') = \pi E_1(x, y) + i \int_{-Y}^Y \frac{E_1(t, y)}{t-x} e^{i c' (t-x)} dt; \quad (2.3)$$

here

$$Y = \sqrt{1-y^2}, \quad c' = \frac{2\pi}{\lambda s} c, \quad (2.4)$$

s is the radius of curvature of M_0 , and the integral in (2.3) is a Cauchy principal value when $-1 < x < 1$. When $|y| > 1$, the value of $D_1(x, y; c')$ is zero.

A change in the figure of the mirror can be expressed by adding to $\phi(x, y)$ a deviation-contribution $\psi(x, y)$, to give the new wave-function

$$\begin{aligned} E(x, y) &= E_1(x, y) e^{2\pi i \psi(x, y)} \\ &= E_1(x, y) (1 + 2\pi i \eta(x, y)), \end{aligned} \quad (2.5)$$

where
$$\eta(x, y) = \frac{1}{2\pi i} (e^{2\pi i \psi(x, y)} - 1). \quad (2.6)$$

We suppose that $\psi(x, y)$ possesses continuous partial differential coefficients everywhere, that $\psi(x, y) \ll 1$ and that $\psi^2(x, y)$ can be neglected. Then $\eta(x, y)$ possesses continuous partial differential coefficients; and, to the same order of approximation as before, $\eta(x, y) = \psi(x, y)$, $\eta(x, y)$ is real, and $\eta^2(x, y)$ can be neglected.

We suppose further that the integral

$$T(x, y) = \int_{-Y}^Y \left| \frac{\eta(t, y) - \eta(x, y)}{t - x} \right| dt \quad (2.7)$$

is, for $x^2 + y^2 < 1$, so small that its square can be neglected. This means, broadly speaking, that the changes in profile are not too violent.

The intensity seen on the mirror under the Foucault test, with the knife-edge at the same setting as before, is now

$$I(x, y; c') = |2\pi D(x, y; c')|^2, \quad (2.8)$$

where

$$\begin{aligned} 2\pi D(x, y; c') &= \pi E(x, y) + i \int_{-Y}^Y \frac{E(t, y)}{t - x} e^{ic'(t-x)} dt \\ &= 2\pi D_1(x, y; c') + \pi \cdot 2\pi i \eta(x, y) E_1(x, y) - 2\pi \int_{-Y}^Y \frac{\eta(t, y) E_1(t, y)}{t - x} e^{ic'(t-x)} dt, \end{aligned} \quad (2.9)$$

by (2.5). Therefore

$$\begin{aligned} |2\pi D(x, y; c')|^2 &= |2\pi D_1(x, y; c')|^2 \\ &+ \left| 2\pi D_1(x, y; c') 2\pi i \eta(x, y) - 2\pi \int_{-Y}^Y \frac{\eta(t, y) - \eta(x, y)}{t - x} E_1(t, y) e^{ic'(t-x)} dt \right|^2 \\ &+ 2\Re \left\{ 2\pi \overline{D_1(x, y; c')} \left[\pi \cdot 2\pi i \eta(x, y) E_1(x, y) - 2\pi \int_{-Y}^Y \frac{\eta(t, y) E_1(t, y)}{t - x} e^{ic'(t-x)} dt \right] \right\}. \end{aligned}$$

Since
$$\left| \int_{-Y}^Y \frac{\eta(t, y) - \eta(x, y)}{t - x} E_1(t, y) e^{ic'(t-x)} dt \right| \leq T(x, y),$$

the second term on the right can be neglected provided that x is not near the edge of the mirror,* and we obtain the approximate formula

$$\begin{aligned} I(x, y; c') - I_1(x, y; c') &= 2\Re \left\{ 2\pi \overline{D_1(x, y; c')} \left[2i\pi^2 \eta(x, y) E_1(x, y) - 2\pi \int_{-Y}^Y \frac{\eta(t, y) E_1(t, y)}{t - x} e^{ic'(t-x)} dt \right] \right\} \quad (2.10) \end{aligned}$$

for the changes in the intensities of the knife-edge shadows which result when an arbitrary small change of $\eta(x, y)$ fringes is made in the figure of the mirror.

* $D_1(x, y; c')$ becomes large near $x = \pm Y$.

The effect of introducing small errors on a previously true mirror is obtained as a special case on setting $\phi(x, y) = 0$. In this case,

$$E_1(x, y) = 1, \quad 2\pi I_1(x, y) = \pi + i \int_{-Y}^Y \frac{e^{ic'(t-x)}}{t-x} dt \quad (2.11)$$

for $x^2 + y^2 < 1$, and (2.10) gives, for these values of x and y ,

$$\begin{aligned} & I(x, y; c') - I_0(x, y; c') \\ &= 2\Re \left\{ \left(\pi - i \int_{-Y}^Y \frac{e^{-ic'(t-x)}}{t-x} dt \right) \left(2i\pi^2 \eta(x, y) - 2\pi \int_{-Y}^Y \frac{\eta(t, y)}{t-x} e^{ic'(t-x)} dt \right) \right\} \\ &= -4\pi \left(\pi - \int_{-Y}^Y \frac{\sin c'(t-x)}{t-x} dt \right) \int_{-Y}^Y \frac{\eta(t, y)}{t-x} \cos c'(t-x) dt \\ &\quad + 2 \int_{-Y}^Y \frac{\cos c'(t-x)}{t-x} dt \left(2\pi^2 \eta(x, y) - 2\pi \int_{-Y}^Y \frac{\eta(t, y)}{t-x} \sin c'(t-x) dt \right); \\ &\frac{1}{4\pi^2} [I(x, y; c') - I_0(x, y; c')] = C(x, y) \left[\pi \eta(x, y) - \int_{-Y}^Y \frac{\eta(t, y)}{t-x} \sin c'(t-x) dt \right] \\ &\quad - [1 - S(x, y)] \int_{-Y}^Y \frac{\eta(t, y)}{t-x} \cos c'(t-x) dt, \quad (2.12) \end{aligned}$$

where

$$Y = \sqrt{1 - y^2}, \quad c' = 2\pi c / \lambda s,$$

$$\begin{aligned} C(x, y) &= \frac{1}{\pi} \int_{-Y}^Y \frac{\cos c'(u-x)}{u-x} du = -\frac{1}{\pi} [\text{Ci}\{c'(Y+x)\} - \text{Ci}\{c'(Y-x)\}] \\ S(x, y) &= \frac{1}{\pi} \int_{-Y}^Y \frac{\sin c'(u-x)}{u-x} du = \frac{1}{\pi} [\text{Si}\{c'(Y+x)\} + \text{Si}\{c'(Y-x)\}], \quad (2.13) \end{aligned}$$

while

$$I_0(x, y; c') = \pi^2 \{ [C(x, y)]^2 + [1 - S(x, y)]^2 \} \quad (2.14)$$

represents the intensities seen on the surface of a true mirror at the same knife-edge setting. The condition (2.7) is always satisfied if the slopes of the 'error-surface' $z = \eta(x, y)$ are everywhere small enough for their squares to be neglected; that is, it is satisfied by small, slow errors of arbitrary form.

3. LOCAL ZONAL ERRORS

To discuss the appearance of a narrow local zone under the test, suppose that $\psi(x, y)$ is radially symmetrical and that it vanishes outside the zone of width 2δ and mean radius r .

During the removal of zonal error from surfaces of nearly perfect revolution-symmetry, attention is usually concentrated on the 'main diameter' of the surface (that is, the diameter running at right angles to the direction of the knife-edge) and the form of the zonal error is inferred from the intensities seen along this diameter. These intensities are obtained on setting $y = 0$ in (2.10). In the case of a local

zone, where $\eta(x, 0)$ is zero everywhere outside the ranges $-r-\delta \leq x \leq -r+\delta$ and $r-\delta \leq x \leq r+\delta$, they satisfy the relation

$$I(x, 0; c') - I_1(x, 0; c') = 2\Re \left\{ 2\pi \overline{D_1(x, 0; c')} \left[2i\pi^2 \eta(x, 0) E_1(x, 0) - 2\pi \left(\int_{-r-\delta}^{-r+\delta} + \int_{r-\delta}^{r+\delta} \right) \frac{\eta(t, 0) E_1(t, 0)}{t-x} e^{ic'(t-x)} dt \right] \right\} \quad (3.1)$$

provided that x is not too close to the ends of the diameter.

If $E_1(x, 0)$ and $D_1(x, 0; c')$ are nearly constant as x varies on and near the zone, (3.1) can be replaced there by the approximate equation

$$I(x, 0; c') - I_1(x, 0; c') = 4\pi^2 \Re \left\{ \overline{D_1(x, 0; c')} \left[2\pi i \eta(x, 0) E_1(\rho, 0) - 2 \left(E_1(-r, 0) \int_{-r-\delta}^{-r+\delta} + E_1(r, 0) \int_{r-\delta}^{r+\delta} \right) \frac{\eta(t, 0)}{t-x} e^{ic'(t-x)} dt \right] \right\}, \quad (3.2)$$

where $\rho = \pm r$ according as $x > 0$ or $x < 0$.

In particular, (3.2) can be used when $\delta \ll 1$ and $E_1(x, 0)$ varies only slowly over the whole range $-1 < x < 1$; that is to say, in the case of a narrow local zone on a nearly true mirror. In this case, the distance (approximately 10 c' -units) through which the knife-edge must be moved laterally to change the appearance of the main part of the mirror from 'fully lit' to 'fully dark' is small compared with the horizontal resolving power of each of the two segments $-r-\delta \leq t \leq -r+\delta$ and $r-\delta \leq t \leq r+\delta$ cut off by the zone on the main diameter, and the value of $e^{ic'(t-x)}$ is accordingly nearly constant over these two t -ranges for the relevant values of c' and of x .

To make the hypotheses more definite, we agree to say that x is 'on or near' the zone when it satisfies one of the two conditions

$$|x-r| \leq 6\delta, \quad (3.3)$$

$$|x+r| \leq 6\delta. \quad (3.4)$$

For such values of x ,

$$\begin{aligned} & \int_{-1}^1 \frac{\eta(t, 0)}{t-x} E_1(t, 0) e^{ic'(t-x)} dt \\ &= E_1(r, 0) e^{ic'(r-x)} \int_{r-\delta}^{r+\delta} \frac{\eta(t, 0)}{t-x} dt + E_1(-r, 0) e^{-ic'(r+x)} \int_{-r-\delta}^{-r+\delta} \frac{\eta(t, 0)}{t-x} dt \end{aligned} \quad (3.5)$$

approximately. When x satisfies (3.3), the second term on the right of (3.5) is small in comparison with the first; when x satisfies (3.4), the first is small in comparison with the second. In either case, (3.5) can be replaced by the equation

$$\int_{-1}^1 \frac{\eta(t, 0) E_1(t, 0)}{t-x} e^{ic'(t-x)} dt = E_1(\rho, 0) \int_{-1}^1 \frac{\zeta(\tau)}{\tau-\xi} d\tau,$$

where

$$\rho = r \operatorname{sgn} x, \quad \xi = \frac{x-\rho}{\delta}, \quad \tau = \frac{t-\rho}{\delta}, *$$

* $\operatorname{sgn} x$ is defined as 1, 0, -1 according as $x > 0$, $= 0$, < 0 .

and the function

$$\zeta(\tau) = \eta(t, 0)$$

expresses the zone-profile in terms of the new variable τ , which runs from -1 to $+1$ on a zonal segment of width 2δ .

(3.2) then gives, for points x on or near the zone,

$$\begin{aligned} & \frac{1}{4\pi^2} \{I(x, 0; c') - I_1(x, 0; c')\} \\ &= \Re \left\{ \overline{D_1(\rho, 0; c')} E_1(\rho, 0) \left[2\pi i \zeta(\xi) - 2 \int_{-1}^1 \frac{\zeta(\tau)}{\tau - \xi} d\tau \right] \right\} \\ &= -\zeta(\xi) \Im \{ 2\pi \overline{D_1(\rho, 0; c')} E_1(\rho, 0) \} - \int_{-1}^1 \frac{\zeta(\tau)}{\tau - \xi} d\tau \Re \{ 2\overline{D_1(\rho, 0; c')} E_1(\rho, 0) \}. \quad (3.6) \end{aligned}$$

In the special case of a narrow local zone on an otherwise true mirror, (3.6) becomes, in virtue of (2.11),

$$\begin{aligned} \frac{1}{4\pi^2} \{I(x, 0; c') - I_1(x, 0; c')\} &= -[\text{Ci}\{|c'(1+\rho)|\} - \text{Ci}\{|c'(1-\rho)|\}] \zeta(\xi) \\ &\quad - \left(1 - \frac{1}{\pi} [\text{Si}\{c'(1+\rho)\} + \text{Si}\{c'(1-\rho)\}] \right) \int_{-1}^1 \frac{\zeta(\tau)}{\tau - \xi} d\tau, \quad (3.7) \end{aligned}$$

a result which can also be derived from (2.12). When the knife-edge is centrally set ($c' = 0$), (3.7) takes the simpler form

$$\frac{1}{4\pi^2} \{I(x, 0; 0) - I_1(x, 0; 0)\} = -\text{sgn } x \log \frac{1+r}{1-r} \zeta(\xi) - \int_{-1}^1 \frac{\zeta(\tau)}{\tau - \xi} d\tau. \quad (3.8)$$

In the more general case where small, slow irregular errors may also be present on the mirror, we write

$$E_1(x, y) = e^{2\pi i \phi(x, y)} = 1 + 2\pi i \eta_1(x, y),$$

and suppose $\phi(x, y)$ so small that its square can be neglected. Then $\eta_1(x, y) = \phi(x, y)$ to the same order of approximation, and an application of (2.9), with

$$2\pi D_0(x, 0; c') = \pi + i \int_{-1}^1 \frac{e^{ic'(t-x)}}{t-x} dt, \quad (3.9)$$

in place of $2\pi D_1$ and with D_1 in place of D , gives

$$2\pi D_1(x, 0; c') = 2\pi D_0(x, 0; c') E_1(x, 0) - 2\pi \int_{-1}^1 \frac{\eta_1(t, 0) - \eta_1(x, 0)}{t-x} e^{ic'(t-x)} dt, \quad (3.10)$$

$$\begin{aligned} 2\pi \overline{D_1(x, 0; c')} E_1(x, 0) &= 2\pi D_0(x, 0; c') |E_1(x, 0)|^2 \\ &\quad - 2\pi E_1(x, 0) \int_{-1}^1 \frac{\eta_1(t, 0) - \eta_1(x, 0)}{t-x} e^{ic'(t-x)} dt. \quad (3.11) \end{aligned}$$

Since the irregular errors are assumed to be slow, the integral

$$T(x, 0) = \int_{-1}^1 \left| \frac{\eta_1(t, 0) - \eta_1(x, 0)}{t-x} \right| dt$$

is of the same order of smallness as $\eta_1(x, 0)$ itself, and the product $\eta_1(x, 0) T(x, 0)$ can be neglected. (3.11) therefore gives

$$2\pi \overline{D_1(x, 0; c')} E_1(x, 0) = 2\pi \overline{D_0(x, 0; c')} - 2\pi \int_{-1}^1 \frac{\eta_1(t, 0) - \eta_1(x, 0)}{t - x} e^{-ic'(0-x)} dt, \quad (3.12)$$

and on substituting in (3.6) we obtain

$$\begin{aligned} & \frac{1}{4\pi^2} \{I(x, 0; c') - I_1(x, 0; c')\} \\ &= \zeta(\xi) \left[\int_{-1}^1 \frac{\cos c'(t-\rho)}{t-\rho} dt + 2\pi \int_{-1}^1 \frac{\eta_1(t, 0) - \eta_1(\rho, 0)}{t-\rho} \sin c'(t-\rho) dt \right] \\ & \quad - \int_{-1}^1 \frac{\zeta(\tau)}{\tau - \xi} d\tau \left[1 - \frac{1}{\pi} \int_{-1}^1 \frac{\sin c'(t-\rho)}{t-\rho} dt - 2 \int_{-1}^1 \frac{\eta_1(t, 0) - \eta_1(\rho, 0)}{t-\rho} \cos c'(t-\rho) dt \right]. \end{aligned}$$

The last terms in the two square brackets are respectively less than $2\pi T(\rho, 0)$, $2T(\rho, 0)$ in absolute value; they can therefore be neglected to the present approximation. It follows that (3.7), and its particular case (3.8), remain valid approximations when, in addition to the narrow zonal error described by $\zeta(\tau)$, small irregular slow errors are present on the mirror surface.

4. INTERPRETATION OF THE TEST

Along the main diameter $y = 0$, the inferred error-slope of the mirror on and near a weak, narrow zone is proportional to $I(x, 0; c') - I_1(x, 0; c')$. It varies somewhat as the lateral setting of the knife-edge is varied, although the variations in the shape of the inferred error-profile are not large enough to attract notice in the ordinary use of the test.

When $c' = 0$, i.e. when the knife-edge is central, the inferred error-profile $P(x)$ or $\zeta^*(\xi)$ on the mirror is given, apart from an appropriate scale factor* and an arbitrary additive constant, by the equation

$$P(x) = -\frac{1}{4\pi^2} \int_{-1}^x \{I(x, 0; 0) - I_1(x, 0; 0)\} dx, \quad (4.1)$$

and (3.8) therefore yields, on and near the zone, the approximate formula

$$\begin{aligned} \zeta^*(\xi) = P(x) &= \operatorname{sgn} x \log \frac{1+r}{1-r} \int_{-1}^{\xi} \zeta(u) du + \int_{-1}^{\xi} \left(\int_{-1}^1 \frac{\zeta(u)}{\tau - u} d\tau \right) du \\ &= \operatorname{sgn} x \log \frac{1+r}{1-r} \int_{-1}^{\xi} \zeta(u) du + \int_{-1}^1 \zeta(\tau) \log \frac{1}{|\tau - \xi|} d\tau. \end{aligned} \quad (4.2)$$

* An unknown scale factor is necessarily involved, since the intensities seen under the test with a very small pinhole are determined by the depths of the errors measured in wave-lengths and not by the angular sizes of the error-slopes. Two mirrors of different sizes but the same shape, for example two paraboloids of different sizes but the same focal ratio, therefore show different shadow-intensities under the test.

(4.2) expresses the distortion which the zone-profile undergoes when 'seen' under the Foucault test with the knife-edge centrally set. That is to say, it describes the 'intrinsic error' of the test when applied to a weak, narrow zone of mean radius r on an otherwise nearly true mirror.

The corresponding formula when the knife-edge is non-central is obtained by substituting from (3.7) into (4.1); it is

$$\zeta^*(\xi) = [\text{Ci}\{c'(1+\rho)\} - \text{Ci}\{c'(1-\rho)\}] \int_{-\xi}^{\xi} \zeta(u) du + \left(1 - \frac{1}{\pi} [\text{Si}\{c'(1+\rho)\} + \text{Si}\{c'(1-\rho)\}]\right) \int_{-1}^1 \zeta(\tau) \log \frac{1}{|\tau - \xi|} d\tau. \quad (4.3)$$

Equations (4.2), (4.3) allow some general conclusions to be drawn about the relation between the inferred profile of a weak, narrow zone and its actual profile.

(4.3) can be written

$$\zeta^*(\xi) = A \int_{-1}^1 \zeta(\tau) \log \frac{1}{|\tau - \xi|} d\tau + B \int_{-\xi}^{\xi} \zeta(u) du, \quad (4.4)$$

where the coefficients

$$A = A(\rho, c') = 1 - \frac{1}{\pi} [\text{Si}\{c'(1+\rho)\} + \text{Si}\{c'(1-\rho)\}],$$

$$B = B(\rho, c') = \text{Ci}\{c'(1+\rho)\} - \text{Ci}\{c'(1-\rho)\}, \quad (4.5)$$

depend on $\rho = r \operatorname{sgn} x$ and on c' , but not on δ . It follows that the apparent distortion imposed by the test on the zone-profile is independent of the zone-width; two narrow zones of the same mean radius but of different widths will possess the same inferred profile $\zeta^*(\xi)$ if they possess the same actual profile.

By (4.4), $\zeta^*(\xi)$ is a linear combination of the two functions

$$\zeta^{(1)}(\xi) = \int_{-1}^1 \zeta(\tau) \log \frac{1}{|\tau - \xi|} d\tau, \quad (4.6)$$

and

$$\zeta^{(2)}(\xi) = \int_{-\xi}^{\xi} \zeta(u) du. \quad (4.7)$$

The first of these is a Faltung or 'smear' of $\zeta(\tau)$ by means of the function $\log 1/|\tau|$. Rapid changes in the slope of the zone-profile are smoothed and rounded off by the smearing process, which also 'spreads' the zone, so that $\zeta^{(1)}(\tau)$ does not vanish everywhere outside the interval $-1 < \tau < 1$, as $\zeta(\tau)$ does, but tails off gradually. Figure 1 illustrates this in the particular case

$$\zeta(\tau) = (1 - \tau^2)^2 \quad (-1 < \tau < 1),$$

$$= 0 \quad (\tau^2 \geq 1). \quad (4.8)$$

When the zone has a symmetrical profile, i.e. when $\zeta(\tau)$ is an even function of τ , $\zeta^{(1)}(\tau)$ is likewise an even function and the 'smeared' zone is symmetrical. However, the inferred profile (4.4) is not symmetrical, because of the effect of the term in $\zeta^{(2)}(\xi)$.

The function $\zeta^{(2)}(\xi)$ is constant outside the interval $(-1, 1)$ but its value is not in general the same on both sides of the interval. In the case of a high or low zone, where $\zeta(\tau)$ is of constant sign in $(-1, 1)$, the smeared function $\zeta^{(1)}(\xi)$ is monotonic in each of the ξ -ranges outside this interval; therefore the inferred profile

$$\zeta^*(\xi) = A\zeta^{(1)}(\xi) + B\zeta^{(2)}(\xi)$$

is likewise monotonic in $(-\infty, -1)$ and in $(1, \infty)$, whatever may be the values of A and B . That is to say, at no setting of the knife-edge do maxima or minima of the

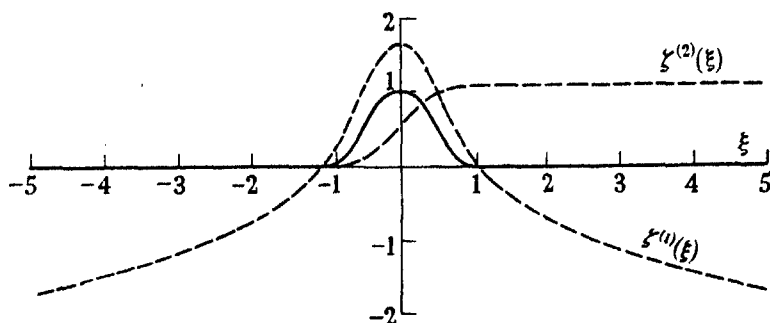


FIGURE 1. The functions $\zeta(\xi)$ (solid curve), $\zeta^{(1)}(\xi)$ and $\zeta^{(2)}(\xi)$ in the case (4.8).

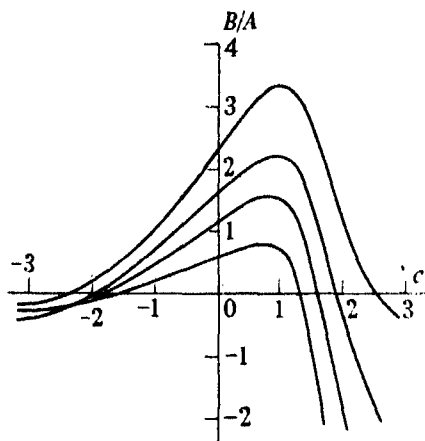


FIGURE 2

inferred zone-profile ever lie outside the actual zone. But their positions within the actual zone vary when the ratio B/A varies; that is, they depend on the lateral setting of the knife-edge and on the situation of the zone on the mirror disk.

The curves in figure 2 show the values of B/A as c' varies, for zones of mean radius 0.25, 0.5, 0.65, 0.80 respectively; the values of c' which are of most practical importance are those between -2 and $+1$ (Linfoot 1946, p. 86; figures 6*a*, *b*). In this range

of values of c' , B/A may be approximated to with sufficient accuracy for practical purposes by the expression $\alpha(\rho)(c' + 2)$, where

$$\alpha(\rho) = 0.25, 0.5, 0.7, 1.1$$

for zones of mean radius 0.25, 0.5, 0.65, 0.80 respectively.

In figure 3 are shown the inferred zone-profiles, calculated from (4.4), corresponding to the actual profile (4.8) in the cases $c' = -1$, $c' = 0$. The value $c' = -1$ corresponds to an approximately 'half-lit' mirror disk and the value $c' = 0$ to a centrally set knife-edge; in the latter case, the disk contains only one-third as much light as with the knife-edge withdrawn (Linfoot 1946, p. 90). It will be seen that the inferred zone spreads well beyond the boundaries of the actual zone and that its crest is displaced outward by an amount which increases as c' increases from -1 to 0. The displacement, though not very noticeable on the inferred profile, amounts to an appreciable fraction of the actual zonal width when $c' = 0$.

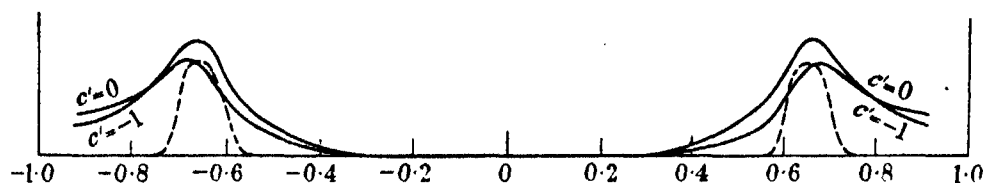


FIGURE 3. Inferred error-profiles (4.4) in the case (4.8). The dotted curves show the shape of the actual error-profile.

The zone 'seen' under the test in practice is a composite impression built up from the inferred profiles for the values of c' which make the zone show up most prominently on the mirror disk, and these values may be taken to lie between -2 and $+1$ when the mirror is nearly true. A ring-polisher made to suit the inferred zone should therefore be found to work rather too much on the outer slopes of the zone and, because it is too broad, should produce a somewhat different effect from that intended. To reduce the zone with greater efficiency, the ring-polisher should be designed to work almost entirely on the central part of the apparent zone and should be set slightly inside the inferred crest-radius.

The well-known difficulty, in correcting mirrors by local polishing with the help of the Foucault test, of preventing the polisher from going outside the limits of the local error under treatment is usually regarded as a difficulty in the manual control of the polisher. According to the present analysis, it may be attributed, in part at least, to the errors inherent in the usual method of interpreting the Foucault shadows.

It is natural to ask how far these conclusions, established only for sufficiently narrow zones of very small height or depth, remain valid as useful approximations when applied to zones of the widths and depths commonly met with in practice. To estimate this, computations of the intensities in four selected special cases were made from the basic formula (2.3), which for practical purposes can be regarded as exact,

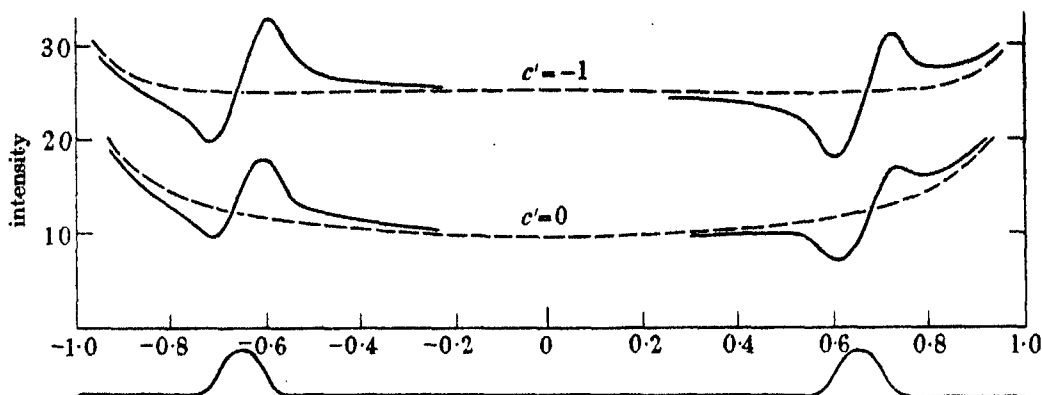


FIGURE 4. Foucault intensities, at two different lateral settings of the knife-edge, for a local zone $\frac{1}{10}$ fringe high. The dotted curves show the intensities for a true mirror. The error-profile is shown below the graph.

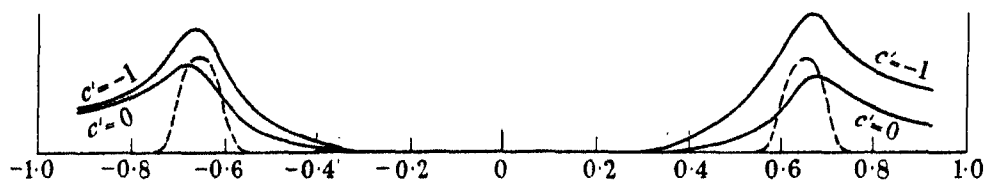


FIGURE 5. Inferred error-profiles corresponding to figure 4. The dotted curves show the shape of the actual error-profile.

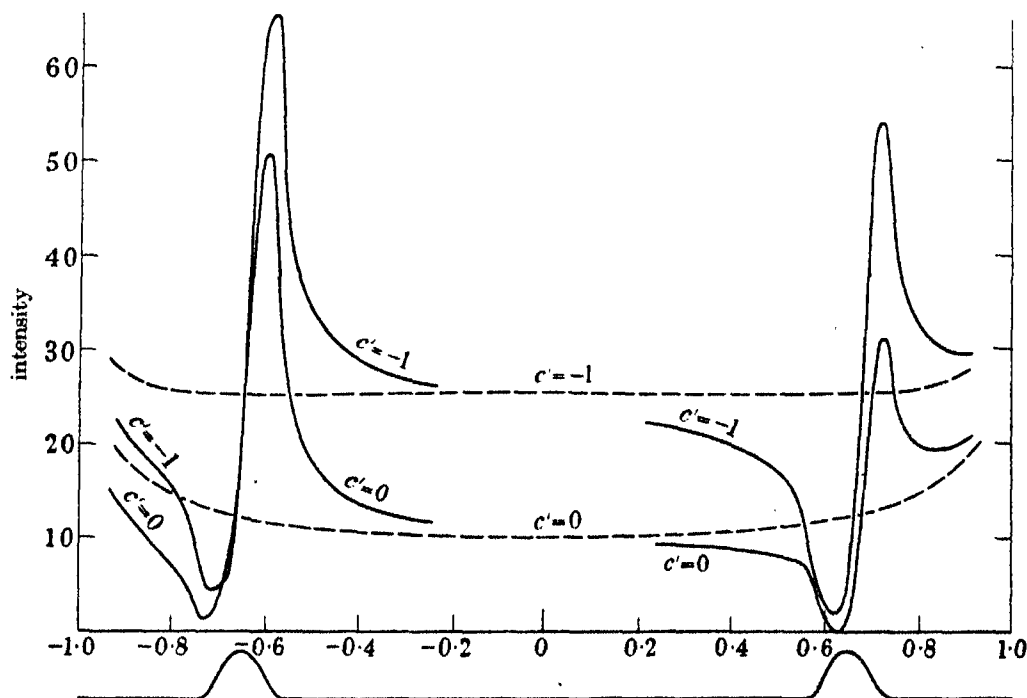


FIGURE 6. Foucault intensities, at two different lateral settings of the knife-edge, for a local zone $\frac{1}{4}$ fringe high. The dotted curves show the intensities for a true mirror. The error-profile is shown below the graph.

and the corresponding inferred profiles were computed from (4.1). There is of course a certain arbitrariness in the use of (4.1) to define the inferred error-profile when the intensity-changes are no longer small.

The four cases selected were high zones of mean radius 0.65, width 0.20, profile shape $\zeta(\tau)$ given by (4.8), and heights $\frac{1}{20}$ fringe and $\frac{1}{4}$ fringe respectively, tested with the knife-edge at the lateral settings $c' = -1$ and $c' = 0$.

Figures 4 and 5 show the results for a zone of height $\frac{1}{20}$ fringe. It will be seen that in this case the inferred profile derived from the approximate formula (4.4) agrees sufficiently well in shape with that derived by computation from the accurate formula (2.3).

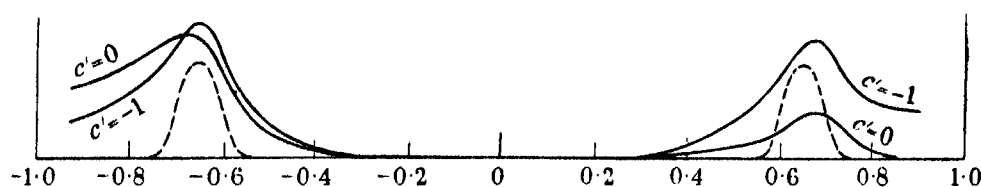


FIGURE 7. Inferred error-profiles corresponding to figure 6. The dotted curves show the shape of the actual error-profile.

The results for a zone of height $\frac{1}{4}$ fringe are shown in figures 6 and 7. Here the inequality between the apparent strengths of the zone on the left- and on the right-hand zonal segments is considerable, and the agreement between (4.4) and the accurate formula is not very close. This is hardly surprising, since the condition that the depth of the zone should be small compared with $\lambda/2\pi$ is far from being satisfied. Even in this case, however, it appears from figure 7 that the general conclusions drawn above retain sufficient validity to be useful to the practical mirror-maker.

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The hydrodynamics of non-Newtonian fluids. I

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The classical theory of the hydrodynamics of viscous fluids depends on the assumption of a particular law governing the relations between the components of stress in a fluid and those of the strain-velocity. This assumption limits its applicability to Newtonian fluids. Here, the most general possible relations between the stress and strain-velocity components, which can be obeyed by an incompressible, visco-inelastic fluid, are derived. These relations also apply to an incompressible, visco-elastic fluid in a steady state of laminar flow. It is shown how equations of motion and boundary conditions can be obtained if these relations are known. Two problems involving laminar flow are then discussed in some detail. These are: (i) the torsional motion of a cylindrical mass of fluid, produced by means of forces applied to its plane ends, and (ii) the laminar flow of a mass of fluid contained between two coaxial cylinders rotating with different angular velocities.

It is found in case (i) that, in general, normal tractions must be applied to the plane surfaces of the fluid, in addition to the azimuthal tractions expected from the classical theory, in order to produce the specified motion. Analogous results are obtained in case (ii). These results apply even when centrifugal forces are neglected and so imply a qualitative difference between the behaviour of fluids in general and those for which the special case of classical hydrodynamics is valid.

1. INTRODUCTION

The classical theory of the hydrodynamics of viscous fluids seeks to answer questions of the following types: (i) If a mass of fluid is subjected to a specified system of forces, what is the resulting flow configuration in the fluid? (ii) What are the forces necessary to produce a specified state of flow in a fluid?

In order to answer these questions, some mathematical description must be given of the fundamental physical properties of the fluid as regards flow. In the classical theory, the assumption is made in the form of a definite relationship between the stress components at a point of the fluid and the strain-velocity components. This relationship is linear, invariant under a transformation of the axes of reference and does not involve time derivatives of the stress or strain-velocity components. From a mathematical point of view, it forms a sufficiently comprehensive description of the basic flow properties of an ideal fluid to form an adequate starting-point for the development of a mathematical theory. The applicability of the results of this theory are, of course, limited by the assumed stress-strain-velocity relationships. The widespread agreement of the predictions of the theory with the experimental results, for such fluids as water, air, mercury, etc., provides justification for it and inspires confidence in its predictions.

It has long been realized, however, that the fundamental stress-strain-velocity relations of classical hydrodynamics are not applicable to a vast number of highly-viscous fluids. Many of these have great technological importance and, with the

growth of scientific investigation of macro-molecular materials and colloids, an increasing scientific interest. To avoid confusion over the use of these terms, it is stated explicitly that, in this paper, fluids will be described as Newtonian or non-Newtonian accordingly as the classical hydrodynamics does or does not apply to them. Non-Newtonian fluids may be either visco-elastic or visco-inelastic.

In the present paper, a hydrodynamic theory is formulated without the restrictions implied by the assumed stress-strain-velocity relations of the classical theory. The only physical assumptions made regarding the fluid are (i) that it is incompressible, (ii) that it is visco-inelastic, and (iii) that it is isotropic when all components of the strain-velocity, as classically defined, are zero.

The mere fact that the material considered is a visco-inelastic fluid implies that the stress-strain-velocity relations do not involve time derivatives of the stress or strain-velocity components. The classical theory, for incompressible fluids, forms a special and simplest case of the theory developed here.

In part A, the kinematics of flow is developed in a form suitable for the purposes of the present theory.

In part B, the most general possible form of the stress-strain-velocity relations, subject to the limitations implied by the assumptions made above, are obtained and the equations of motion and boundary conditions are discussed.

In part C, two simple problems involving steady-state laminar flow are discussed. These are: (i) the torsional motion of a cylindrical mass of fluid, produced by forces applied to the plane ends, and (ii) the torsional motion of a mass of fluid between infinite coaxial cylinders rotating with different angular velocities about their common axis.

In both cases, the relation between the force system and the flow-velocity and the resulting stress distribution in the fluid are derived.

Throughout the paper a rectangular, Cartesian reference system has been used. Much of the discussion could, of course, be readily expressed in the notation of the tensor calculus, but in the interests of ease of application and availability to a wider circle of readers, this has not been done.

A. THE KINEMATICS OF FLOW

2. DESCRIPTION OF A STATE OF STEADY FLOW

Consider a viscous, incompressible fluid in a state of steady flow. The state of flow may be described completely with reference to a fixed rectangular, Cartesian co-ordinate system (x, y, z) . The velocity of a point of the fluid which is at (x, y, z) has components u, v and w parallel to the axes x, y and z respectively. Since the state of flow is steady, u, v and w are functions of x, y and z only and independent of time.

The velocities of two neighbouring points P and P' situated at (x, y, z) and $(x + \delta x, y + \delta y, z + \delta z)$ respectively have components (u, v, w) and $(u + \delta u, v + \delta v, w + \delta w)$

respectively. Then δu , δv and δw are the components of the velocity of P' relative to P . Since u , v and w are functions of x , y and z only, we have

$$\delta u = u_x \delta x + u_y \delta y + u_z \delta z, \quad (2.1)$$

together with two similar equations for δv and δw .

The velocity of P' relative to P can be considered to be made up of two parts:

(i) that due to the pure rotation of the element of volume containing PP' ; this has components $\delta \varpi_1$, $\delta \varpi_2$ and $\delta \varpi_3$, given by

$$\delta \varpi_1 = \frac{1}{2}(\eta \delta z - \zeta \delta y), \quad \delta \varpi_2 = \frac{1}{2}(\zeta \delta x - \xi \delta z) \quad \text{and} \quad \delta \varpi_3 = \frac{1}{2}(\xi \delta y - \eta \delta x), \quad (2.2)$$

$$\text{in which} \quad \xi = w_y - v_z, \quad \eta = u_z - w_x \quad \text{and} \quad \zeta = v_x - u_y; \quad (2.3)$$

(ii) that due to the irrotational deformation of the element of volume containing PP' ; its components $\delta u'$, $\delta v'$ and $\delta w'$ are given by

$$\left. \begin{aligned} \delta u' &= a \delta x + \frac{1}{2} h \delta y + \frac{1}{2} g \delta z, \\ \delta v' &= \frac{1}{2} h \delta x + b \delta y + \frac{1}{2} f \delta z, \\ \delta w' &= \frac{1}{2} g \delta x + \frac{1}{2} f \delta y + c \delta z, \end{aligned} \right\} \quad (2.4)$$

and

where

$$a = u_x, \quad b = v_y, \quad c = w_z, \quad f = v_z + w_y, \quad g = w_x + u_z \quad \text{and} \quad h = u_y + v_x. \quad (2.5)$$

It can readily be seen that

$$\delta u = \delta u' + \delta \varpi_1, \quad \delta v = \delta v' + \delta \varpi_2 \quad \text{and} \quad \delta w = \delta w' + \delta \varpi_3, \quad (2.6)$$

where δu , δv and δw are given by (2.1).

The magnitude δV of the relative velocity (δu , δv , δw) is given by

$$\begin{aligned} (\delta V)^2 &= (\delta u)^2 + (\delta v)^2 + (\delta w)^2 \\ &= A(\delta x)^2 + B(\delta y)^2 + C(\delta z)^2 + F \delta y \delta z + G \delta z \delta x + H \delta x \delta y, \end{aligned} \quad (2.7)$$

where

$$\left. \begin{aligned} A &= u_x^2 + v_x^2 + w_x^2, & F &= 2(u_y u_x + v_y v_x + w_y w_x), \\ B &= u_y^2 + v_y^2 + w_y^2, & G &= 2(u_z u_x + v_z v_x + w_z w_x), \\ C &= u_z^2 + v_z^2 + w_z^2, & H &= 2(u_x u_y + v_x v_y + w_x w_y). \end{aligned} \right\} \quad (2.8)$$

Again, the magnitude $\delta V'$ of the irrotational relative velocity ($\delta u'$, $\delta v'$, $\delta w'$) is given by

$$\begin{aligned} (\delta V')^2 &= (\delta u')^2 + (\delta v')^2 + (\delta w')^2 \\ &= A'(\delta x)^2 + B'(\delta y)^2 + C'(\delta z)^2 + F' \delta y \delta z + G' \delta z \delta x + H' \delta x \delta y, \end{aligned} \quad (2.9)$$

where

$$\left. \begin{aligned} A' &= a^2 + \frac{1}{4}(g^2 + h^2), & F' &= \frac{1}{2}gh + (b+c)f, \\ B' &= b^2 + \frac{1}{4}(h^2 + f^2), & G' &= \frac{1}{2}hf + (c+a)g, \\ C' &= c^2 + \frac{1}{4}(f^2 + g^2), & H' &= \frac{1}{2}fg + (a+b)h, \end{aligned} \right\} \quad (2.10)$$

and a , b , c , f , g and h are given by (2.5).

Since the length δs of the element PP' is given by

$$(\delta s)^2 = (\delta x)^2 + (\delta y)^2 + (\delta z)^2, \quad (2.11)$$

and its direction-cosines (l, m, n) by

$$l = \delta x / \delta s, \quad m = \delta y / \delta s \quad \text{and} \quad n = \delta z / \delta s, \quad (2.12)$$

we obtain, from (2.7),

$$(dV/ds)^2 = (\delta V/\delta s)^2 = Al^2 + Bm^2 + Cn^2 + Fmn + Gnl + Hlm, \quad (2.13)$$

and, from (2.9),

$$(dV'/ds)^2 = (\delta V'/\delta s)^2 = A'l'^2 + B'm'^2 + C'n'^2 + F'mn + G'nl + H'lm. \quad (2.14)$$

If θ is the angle between the directions of the relative velocity $(\delta u, \delta v, \delta w)$ and the linear element PP' , we have

$$\begin{aligned} \delta V \delta s \cos \theta &= \delta x \delta u + \delta y \delta v + \delta z \delta w \\ &= a(\delta x)^2 + b(\delta y)^2 + c(\delta z)^2 + f\delta y \delta z + g\delta z \delta x + h\delta x \delta y. \end{aligned} \quad (2.15)$$

Thus, employing the relations (2.11), (2.12) and (2.15), we have

$$\begin{aligned} (dV/ds) \cos \theta &= (\delta V/\delta s) \cos \theta \\ &= al^2 + bm^2 + cn^2 + fmn + gnl + hlm. \end{aligned} \quad (2.16)$$

If θ' is the angle between the irrotational relative velocity $(\delta u', \delta v', \delta w')$ and the element PP' , we can similarly obtain

$$\delta V' \delta s \cos \theta' = a(\delta x)^2 + b(\delta y)^2 + c(\delta z)^2 + f\delta y \delta z + g\delta z \delta x + h\delta x \delta y, \quad (2.17)$$

or

$$\begin{aligned} (dV'/ds) \cos \theta' &= (\delta V'/\delta s) \cos \theta' \\ &= al^2 + bm^2 + cn^2 + fmn + gnl + hlm. \end{aligned} \quad (2.18)$$

3. THE FLOW QUADRICS

If we consider a small element of the fluid in the neighbourhood of the point (x, y, z) and take $(\delta x, \delta y, \delta z)$ as the current co-ordinates of a point P' in this element, in the co-ordinate system $(\delta x, \delta y, \delta z)$ whose origin P is at (x, y, z) and whose axes are parallel to those of the original reference axes (x, y, z) , then equation (2.7), in which δV is given some constant value, represents the surface on which the velocity of P' relative to P has this value. We can choose the axes of reference (x, y, z) —and hence $(\delta x, \delta y, \delta z)$ —to be parallel to the axes of this quadric. The axes of reference will, of course, then vary in direction from point to point of the fluid. With this choice of axes the equation of the quadric takes the form

$$V_1^2(\delta x)^2 + V_2^2(\delta y)^2 + V_3^2(\delta z)^2 = (\delta V)^2, \quad (3.1)$$

where V_1^2 , V_2^2 and V_3^2 are the values of V^2 given by

$$\begin{vmatrix} A - V^2 & \frac{1}{2}H & \frac{1}{2}G \\ \frac{1}{2}H & B - V^2 & \frac{1}{2}F \\ \frac{1}{2}G & \frac{1}{2}F & C - V^2 \end{vmatrix} = 0. \quad (3.2)$$

If we put $\delta y = \delta z = 0$ in (3.1), we obtain

$$(\delta V)^2 = V_1^2(\delta x)^2.$$

Thus, V_1^2 is inherently positive. Analogously, V_2^2 and V_3^2 are positive. Therefore, the quadric represented by equation (3.1) or (2.7) is an ellipsoid.

The lengths of the semi-axes of the flow ellipsoid (3.1) or (2.7) are proportional to $1/V_1$, $1/V_2$ and $1/V_3$ and it should be noted that the motion of the element of fluid in the neighbourhood of P —apart from any translational motion of the element as a whole—may be considered to consist of three components of relative motion, parallel to the axes of the ellipsoid (3.1). These components are V_1 , V_2 and V_3 per unit length in the appropriate direction.

In a similar manner, equation (2.9), in which $\delta V'$ has some constant value, represents a surface on which the irrotational portion of the velocity of P' relative to P , has the value $\delta V'$. Again, we can choose the axes of reference to be parallel to the axes of the ellipsoid (2.9). Then, equation (2.9) takes the form

$$V_1'^2(\delta x)^2 + V_2'^2(\delta y)^2 + V_3'^2(\delta z)^2 = (\delta V')^2, \quad (3.3)$$

where $V_1'^2$, $V_2'^2$ and $V_3'^2$ are the values of V'^2 given by

$$\begin{vmatrix} A' - V'^2 & \frac{1}{2}H' & \frac{1}{2}G' \\ \frac{1}{2}H' & B' - V'^2 & \frac{1}{2}F' \\ \frac{1}{2}G' & \frac{1}{2}F' & C' - V'^2 \end{vmatrix} = 0. \quad (3.4)$$

As in the case of equation (2.7), it can be seen that the quadric represented by (3.3) is an ellipsoid.

The lengths of the semi-axes of the flow ellipsoid (2.9) or (3.3) are proportional to $1/V_1'$, $1/V_2'$ and $1/V_3'$. Again, it is noted that the irrotational portion of the motion in the fluid element in the neighbourhood of P may be considered to consist of three components of relative motion, parallel to the axes of the ellipsoid (2.9). These components are V_1' , V_2' and V_3' per unit length in their directions.

Again, let us consider the flow quadric (2.17). Transforming this to its axes as axes of reference, it takes the form

$$U_1(\delta x)^2 + U_2(\delta y)^2 + U_3(\delta z)^2 = \delta V' \delta s \cos \theta', \quad (3.5)$$

where U_1 , U_2 and U_3 are the values of u given by

$$\begin{vmatrix} a - U & \frac{1}{2}h & \frac{1}{2}g \\ \frac{1}{2}h & b - U & \frac{1}{2}f \\ \frac{1}{2}g & \frac{1}{2}f & c - U \end{vmatrix} = 0. \quad (3.6)$$

It can be seen that the direction of the velocity $\delta V'$ at any point of the surface of the quadric (2.17) or (3.5) is that of the normal to the quadric at that point.

4. SCALAR INVARIANTS OF THE STATE OF FLOW

From equation (3.2), we see that V_1^2 , V_2^2 and V_3^2 are the values of V^2 for which the equation

$$V^6 - I_1 V^4 + I_2 V^2 - I_3 = 0, \quad (4.1)$$

in which

$$\left. \begin{aligned} I_1 &= A + B + C, \\ I_2 &= AB + BC + CA - \frac{1}{4}F^2 - \frac{1}{4}G^2 - \frac{1}{4}H^2 \\ I_3 &= ABC + \frac{1}{4}FGH - \frac{1}{4}AF^2 - \frac{1}{4}BG^2 - \frac{1}{4}CH^2, \end{aligned} \right\} \quad (4.2)$$

and

is satisfied,

Thus, we have

$$\left. \begin{aligned} I_1 &= V_1^2 + V_2^2 + V_3^2, \\ I_2 &= V_1^2 V_2^2 + V_2^2 V_3^2 + V_3^2 V_1^2 \\ I_3 &= V_1^2 V_2^2 V_3^2. \end{aligned} \right\} \quad (4.3)$$

and

Since the solutions of (4.1) for V^2 are independent of the choice of the axes of reference, any symmetrical function of V_1^2 , V_2^2 and V_3^2 must be independent of the choice of the axes of reference and must therefore be a scalar invariant of the flow with respect to a transformation of axes. In particular, the three independent functions of V_1^2 , V_2^2 and V_3^2 , given by equations (3.2) or (4.1), must be scalar invariants of the flow. This could be directly proved by carrying out the transformation of the expressions on the right-hand side of equations (4.2) from one rectangular, Cartesian co-ordinate system to another, bearing in mind that A , B , C , F , G and H are defined, in any rectangular, Cartesian co-ordinate system, by (2.8).

Again, by writing equation (3.4) in the form

$$V'^6 - J_1 V'^4 + J_2 V'^2 - J_3 = 0, \quad (4.4)$$

where

$$\left. \begin{aligned} J_1 &= A' + B' + C', \\ J_2 &= A'B' + B'C' + C'A' - \frac{1}{4}F'^2 - \frac{1}{4}G'^2 - \frac{1}{4}H'^2 \\ J_3 &= A'B'C' + \frac{1}{4}F'G'H' - \frac{1}{4}A'F'^2 - \frac{1}{4}B'G'^2 - \frac{1}{4}C'H'^2, \end{aligned} \right\} \quad (4.5)$$

and

we readily see that if $V_1'^2$, $V_2'^2$ and $V_3'^2$ are the values of V'^2 for which equation (4.4) is satisfied,

$$\left. \begin{aligned} J_1 &= V_1'^2 + V_2'^2 + V_3'^2, \\ J_2 &= V_1'^2 V_2'^2 + V_2'^2 V_3'^2 + V_3'^2 V_1'^2 \\ J_3 &= V_1'^2 V_2'^2 V_3'^2. \end{aligned} \right\} \quad (4.6)$$

and

By an argument similar to that used in establishing the invariance of I_1 , I_2 and I_3 , it can be seen that J_1 , J_2 and J_3 , given by (4.5) or (4.6), are independent scalar invariants of the flow.

Again, by writing by equation (3.6) in the form

$$U^3 - K_1 U^2 + K_2 U - K_3 = 0, \quad (4.7)$$

where

$$\left. \begin{aligned} K_1 &= U_1 + U_2 + U_3 = a + b + c, \\ K_2 &= U_1 U_2 + U_2 U_3 + U_3 U_1 = ab + bc + ca - \frac{1}{4}f^2 - \frac{1}{4}g^2 - \frac{1}{4}h^2 \\ K_3 &= U_1 U_2 U_3 = abc + \frac{1}{4}fgh - \frac{1}{4}af^2 - \frac{1}{4}bg^2 - \frac{1}{4}ch^2, \end{aligned} \right\} \quad (4.8)$$

and

we can establish that K_1 , K_2 and K_3 are independent scalar invariants of the flow. U_1 , U_2 , U_3 are the values of U for which equation (4.7) is satisfied.

5. RELATIONS BETWEEN THE SCALAR INVARIANTS OF FLOW

In this section we shall state certain relationships between the scalar invariants of flow K_1 , K_2 and K_3 , defined by (4.8), and the scalar invariants of flow J_1 , J_2 and J_3 , defined by (4.5).

The relations are

$$J_1 = -2K_2 + K_1^2, \quad J_2 = K_2^2 - 2K_1K_3 \quad \text{and} \quad J_3 = K_3^2. \quad (5.1)$$

These may be readily proved by employing equations (4.8) to express K_1 , K_2 and K_3 in terms of a , b , c , f , g and h and equations (4.5), together with equations (2.10), to express J_1 , J_2 and J_3 in terms of a , b , c , f , g and h . By simple algebraic manipulation, the relations (5.1) are derived.

If the fluid is incompressible, it can readily be shown (see, for example, Lamb (1924, § 12)), that

$$K_1 = a + b + c = 0. \quad (5.2)$$

In this case, the relationships (5.1) become

$$J_1 = -2K_2, \quad J_2 = K_2^2 \quad \text{and} \quad J_3 = K_3^2. \quad (5.3)$$

The following further relationship, which is readily proved, by simple algebraic manipulation, from (2.10) and (4.8), is worthy of note:

$$aA' + bB' + cC' + \frac{1}{2}fF' + \frac{1}{2}gG' + \frac{1}{2}hH' = K_1^3 - 3K_1K_2 + 3K_3. \quad (5.4)$$

If the fluid is incompressible, so that the relation (5.2) is obeyed, equation (5.4) becomes

$$aA' + bB' + cC' + \frac{1}{2}fF' + \frac{1}{2}gG' + \frac{1}{2}hH' = 3K_3. \quad (5.5)$$

6. RELATIONS BETWEEN THE AXES OF THE FLOW QUADRICS

In this section we shall first prove that

$$V_1'^2 = U_1^2, \quad V_2'^2 = U_2^2 \quad \text{and} \quad V_3'^2 = U_3^2, \quad (6.1)$$

where V_1' , V_2' and V_3' and U_1 , U_2 and U_3 are defined as in § 3. Then, it will be shown that the axes of the flow quadrics (2.9) and (2.17), at any point, are parallel.

Squaring equation (4.7), we have

$$U^6 - 2K_1U^5 + (K_1^2 + 2K_2)U^4 - (2K_3 + 2K_1K_2)U^3 + (2K_1K_3 + K_2^2)U^2 - 2K_2K_3U + K_3^2 = 0. \quad (6.2)$$

From (4.7), $U^3 = K_1U^2 - K_2U + K_3$.

Introducing this expression for U^3 in the term of (6.2) in U^5 , we have

$$U^6 - (K_1^2 - 2K_2)U^4 - 2K_3U^3 + K_2^2U^2 - 2K_2K_3U + K_3^2 = 0. \quad (6.3)$$

Again, from (4.7), $K_2U = K_1U^2 + K_3 - U^3$.

Employing this to substitute for K_2U in the term $-2K_2K_3U$ of (6.3), we obtain

$$U^6 - (K_1^2 - 2K_2)U^4 + (K_2^2 - 2K_1K_3)U^2 - K_3^2 = 0. \quad (6.4)$$

Introducing into (6.4) the relations (5.1), we obtain

$$U^6 - J_1 U^4 + J_2 U^2 - J_3 = 0. \quad (6.5)$$

Comparing equations (6.5) and (4.4), it can readily be seen that the values of U^2 for which equation (6.5) is satisfied are equal to the values of V'^2 for which equation (4.4) is satisfied. Now, since equation (6.5) is obtained by squaring (4.7), the values U_1 , U_2 and U_3 of U which satisfy (4.7) also satisfy (6.5). Thus, we obtain the relations (6.1).

Let (l_1, m_1, n_1) be the direction-cosines of an axis of the flow ellipsoid (2.17) with respect to the co-ordinate system (x, y, z) . Then, if U_1 is the value of U for this axis, l_1 , m_1 and n_1 are given by

$$\left. \begin{aligned} (a - U_1)l_1 + \frac{1}{2}hm_1 + \frac{1}{2}gn_1 &= 0, \\ \frac{1}{2}hl_1 + (b - U_1)m_1 + \frac{1}{2}fn_1 &= 0 \\ \frac{1}{2}gl_1 + \frac{1}{2}fm_1 + (c - U_1)n_1 &= 0. \end{aligned} \right\} \quad (6.6)$$

and

Multiplying these three equations by a , $\frac{1}{2}h$ and $\frac{1}{2}g$ respectively and adding, bearing in mind the relations (2.10), we obtain

$$A'l_1 + \frac{1}{2}H'm_1 + \frac{1}{2}G'n_1 - U_1(al_1 + \frac{1}{2}hm_1 + \frac{1}{2}gn_1) = 0. \quad (6.7)$$

Substituting from the first of equations (6.6) in (6.7), we obtain

$$(A' - U_1^2)l_1 + \frac{1}{2}H'm_1 + \frac{1}{2}G'n_1 = 0.$$

Introducing into this equation the first of the results (6.1), we obtain

$$(A' - V_1'^2)l_1 + \frac{1}{2}H'm_1 + \frac{1}{2}G'n_1 = 0. \quad (6.8)$$

In an analogous manner, we can obtain the further equations

$$\left. \begin{aligned} \frac{1}{2}H'l_1 + (B' - V_1'^2)m_1 + \frac{1}{2}F'n_1 &= 0 \\ \frac{1}{2}G'l_1 + \frac{1}{2}F'm_1 + (C' - V_1'^2)n_1 &= 0. \end{aligned} \right\} \quad (6.9)$$

and

Now, equations (6.8) and (6.9) are the equations determining the direction-cosines (l_1, m_1, n_1) of an axis of the ellipsoid (2.9) with respect to x, y, z . Thus, the flow quadrics (2.9) and (2.17) must have their axes parallel.

7. TRANSFORMATION OF THE STRAIN-VELOCITY COMPONENTS

If the rectangular, Cartesian co-ordinate systems (x, y, z) and (x_0, y_0, z_0) are oriented with respect to each other according to the scheme

$$\begin{array}{c|ccc} & x & y & z \\ \hline x_0 & l_1 & m_1 & n_1 \\ y_0 & l_2 & m_2 & n_2 \\ z_0 & l_3 & m_3 & n_3 \end{array}$$

then

$$\left. \begin{aligned} x_0 &= l_1 x + m_1 y + n_1 z, \\ y_0 &= l_2 x + m_2 y + n_2 z, \\ z_0 &= l_3 x + m_3 y + n_3 z. \end{aligned} \right\} \quad (7.1)$$

and

If (u_0, v_0, w_0) are the velocity components in the co-ordinate system (x_0, y_0, z_0) corresponding to the velocity components (u, v, w) in the co-ordinate system (x, y, z) , we have

$$\left. \begin{aligned} u &= l_1 u_0 + l_2 v_0 + l_3 w_0, \\ v &= m_1 u_0 + m_2 v_0 + m_3 w_0 \\ w &= n_1 u_0 + n_2 v_0 + n_3 w_0. \end{aligned} \right\} \quad (7.2)$$

and

Now, employing the relations (7.1) and (7.2), the six equations relating

$$(a, b, c, \tfrac{1}{2}f, \tfrac{1}{2}g, \tfrac{1}{2}h) \quad \text{and} \quad (a_0, b_0, c_0, \tfrac{1}{2}f_0, \tfrac{1}{2}g_0, \tfrac{1}{2}h_0)$$

can be obtained as

$$\left. \begin{aligned} a &= u_x = l_1^2 a_0 + l_2^2 b_0 + l_3^2 c_0 + l_2 l_3 f_0 + l_3 l_1 g_0 + l_1 l_2 h_0, \text{ etc.} \\ \tfrac{1}{2}f &= \tfrac{1}{2}(v_x + w_y) = m_1 n_1 a_0 + m_2 n_2 b_0 + m_3 n_3 c_0 + (m_2 n_3 + m_3 n_2)(\tfrac{1}{2}f_0) \\ &\quad + (m_3 n_1 + m_1 n_3)(\tfrac{1}{2}g_0) + (m_1 n_2 + m_2 n_1)(\tfrac{1}{2}h_0), \text{ etc.,} \end{aligned} \right\} \quad (7.3)$$

where $a_0, b_0, c_0, \tfrac{1}{2}f_0, \tfrac{1}{2}g_0, \tfrac{1}{2}h_0$ are the components of the strain-velocity in the co-ordinate system (x_0, y_0, z_0) ; i.e. $a_0 = \partial u_0 / \partial x_0$, etc.

In (7.3) the expressions for b and $\tfrac{1}{2}g$ are obtained from those for a and $\tfrac{1}{2}f$ by replacing l by m , m by n and n by l . Those for c and $\tfrac{1}{2}h$ are similarly obtained from the expressions for b and $\tfrac{1}{2}g$.

From the relations (7.3) we can readily find $A', B', C', \tfrac{1}{2}F', \tfrac{1}{2}G'$ and $\tfrac{1}{2}H'$ in terms of $A'_0, B'_0, C'_0, \tfrac{1}{2}F'_0, \tfrac{1}{2}G'_0$ and $\tfrac{1}{2}H'_0$, where

$$A'_0 = a_0^2 + \tfrac{1}{4}(g_0^2 + h_0^2), \text{ etc.} \quad \text{and} \quad F'_0 = \tfrac{1}{2}g_0 h_0 + (b_0 + c_0)f_0, \text{ etc.} \quad (7.4)$$

We obtain

$$\left. \begin{aligned} A' &= l_1^2 A'_0 + l_2^2 B'_0 + l_3^2 C'_0 + 2l_2 l_3 (\tfrac{1}{2}F'_0) + 2l_3 l_1 (\tfrac{1}{2}G'_0) + 2l_1 l_2 (\tfrac{1}{2}H'_0), \text{ etc.} \\ \tfrac{1}{2}F' &= m_1 n_1 A'_0 + m_2 n_2 B'_0 + m_3 n_3 C'_0 + (m_2 n_3 + m_3 n_2)(\tfrac{1}{2}F'_0) \\ &\quad + (m_3 n_1 + m_1 n_3)(\tfrac{1}{2}G'_0) + (m_1 n_2 + m_2 n_1)(\tfrac{1}{2}H'_0), \text{ etc.} \end{aligned} \right\} \quad (7.5)$$

B. THE DYNAMICS OF NON-NEWTONIAN FLUIDS

8. THE DISSIPATION-FUNCTION

If we consider an element, of volume $d\tau$, in the neighbourhood of the point $P(x, y, z)$ of a mass of fluid, then the rate at which energy is dissipated in this volume in the form of heat is $\Phi d\tau$ (say), where Φ is dependent on the state of flow within the element of volume. We shall call Φ the *dissipation-function*.* Now, Φ cannot be dependent on the choice of the axes of reference and must therefore be a scalar invariant of the state of flow.

We have already seen in § 2 that the state of flow may be completely described by specifying a purely rotational velocity for the volume elements in the neighbourhood

* The dissipation-function as defined here is not identical with the Rayleigh dissipation-function. The latter is equal to half the rate at which energy is dissipated per unit volume.

of each point of the fluid together with a velocity of relative separation of the various points of the element. The purely rotational motion of the element involves no relative separation of the points of the fluid and therefore involves no energy dissipation in the element itself.

The dissipation-function Φ is therefore dependent purely on the irrotational component of the flow and is therefore a function of the scalar invariants K_1 , K_2 and K_3 of the irrotational component of the flow. Bearing in mind that for an incompressible fluid $K_1 = 0$, the dissipation-function is then a function of K_2 and K_3 only. Thus,

$$\Phi = \Phi(K_2, K_3). \quad (8.1)$$

Whatever the form of Φ as a function of K_2 and K_3 , it can be approximated, with any desired degree of accuracy, by a polynomial expression. Thus

$$\Phi = \sum_{i=0}^I \sum_{j=0}^J \mu_{ij} K_2^i K_3^j, \quad (8.2)$$

where μ_{ij} are constants characterizing the particular fluid considered. Since, when the fluid is stationary, K_2 , K_3 and Φ must all be zero, $\mu_{00} = 0$.

9. THE RELATION BETWEEN STRESS AND STATE OF FLOW

It has been shown (see, for example, Lamb (1924, § 329)) that the rate Φ at which energy is dissipated, per unit volume of a fluid, is related to the stress components $t_{xx}, t_{yy}, \dots, t_{xy}$ by the formula

$$\Phi = t_{xx}a + t_{yy}b + t_{zz}c + t_{yz}f + t_{zx}g + t_{xy}h. \quad (9.1)$$

The argument leading to this relation is a purely mechanical one and does not involve any assumptions regarding the physical properties of the fluid and so can be taken over here without change.

In developing our hydrodynamic theory for incompressible, visco-inelastic, non-Newtonian fluids, it is now necessary to find a set of relationships between the stress components at a point and the values of the components $a, b, c, \frac{1}{2}f, \frac{1}{2}g, \frac{1}{2}h$ of the strain-velocity, corresponding to any specified dissipation-function. It can readily be seen that although this cannot be done uniquely, the specification of a particular dissipation-function limits the form which can be taken by the stress-strain-velocity relationships, because of the relation (9.1).

Let us consider the stress-strain-velocity relation

$$t_{xx} = 2\mu a + p, \text{ etc.} \quad \text{and} \quad t_{yz} = \mu f, \text{ etc.} \quad (9.2)$$

This is the classical stress-strain-velocity relation for an incompressible, Newtonian fluid. It is readily seen, in view of equations (9.1), (4.8) and (5.2), that for such a fluid

$$\Phi = -4\mu K_2. \quad (9.3)$$

Again, let us consider the stress-strain-velocity relation

$$t_{xx} = 2\mu' A' + p, \text{ etc.} \quad \text{and} \quad t_{yz} = \mu' F', \text{ etc.} \quad (9.4)$$

Then, in view of equations (9.1), (5.5) and (5.2), the corresponding form of the dissipation-function Φ is given by

$$\Phi = 6\mu'K_3. \quad (9.5)$$

For stress-strain-velocity relations having the form (9.2) or (9.4), it is seen that the corresponding dissipation-functions, given by (9.3) and (9.5), are functions of the scalar invariants of flow, K_2 and K_3 .

Generalizing this result, let us consider the stress-strain-velocity relations to have the form

$$t_{xx} = 2\Theta a + 2\Psi A' + p, \text{ etc.} \quad \text{and} \quad t_{yz} = \Theta f + \Psi F', \text{ etc.}, \quad (9.6)$$

where Θ and Ψ are any functions of the scalar invariants of flow K_2 and K_3 . Then, by similar arguments to those employed in deriving equations (9.3) and (9.5) from (9.2) and (9.4) respectively, we obtain the dissipation-function corresponding to the stress-strain-velocity relations (9.6) as

$$\Phi = -4\Theta K_2 + 6\Psi K_3. \quad (9.7)$$

This dissipation-function is clearly a function of the scalar invariants of flow K_2 and K_3 .

Of course, for a set of stress-strain-velocity relations to be admissible as the description of the flow properties of a fluid, they must not only lead to a dissipation-function which is independent of the state of flow, but must also be invariant under a transformation of the axes of reference. It can readily be shown that the relations (9.6) satisfy this condition and this will be done in the next section.

10. INVARIANCE OF THE STRESS-STRAIN-VELOCITY RELATIONS

The stress components $t_{xx}, t_{yy}, \dots, t_{xy}$ transform (see, for example, Love (1927, § 49)) according to the law

$$\left. \begin{aligned} t_{xx} &= l_1^2 t_{x_0 x_0} + l_2^2 t_{y_0 y_0} + l_3^2 t_{z_0 z_0} + 2l_2 l_3 t_{y_0 z_0} + 2l_3 l_1 t_{z_0 x_0} + 2l_1 l_2 t_{x_0 y_0}, \text{ etc.} \\ \text{and} \quad t_{yz} &= m_1 n_1 t_{x_0 x_0} + m_2 n_2 t_{y_0 y_0} + m_3 n_3 t_{z_0 z_0} + (m_2 n_3 + m_3 n_2) t_{y_0 z_0} \\ &\quad + (m_3 n_1 + m_1 n_3) t_{z_0 x_0} + (m_1 n_2 + m_2 n_1) t_{x_0 y_0}, \text{ etc.}, \end{aligned} \right\} \quad (10.1)$$

where $t_{x_0 x_0}, t_{y_0 y_0}, \dots, t_{x_0 y_0}$ are the components of stress in the co-ordinate system (x_0, y_0, z_0) defined as in § 7.

It is readily seen, by comparing equations (10.1) with equations (7.3) and (7.5), that the stress components $t_{xx}, t_{yy}, \dots, t_{xy}$ and the quantities $(a, b, c, \frac{1}{2}f, \frac{1}{2}g, \frac{1}{2}h)$ and $(A', B', C', \frac{1}{2}F', \frac{1}{2}G', \frac{1}{2}H')$ all transform according to the same laws, when the axes of reference are transformed. The stress-strain-velocity relations (9.6) are therefore invariant under a transformation from one set of rectangular, Cartesian co-ordinates to another. It is noted that Θ and Ψ , being functions of the flow invariants, are unaltered by a transformation of the axes. Also, p is unaltered by a transformation of the axes.

It is noteworthy that the law of transformation of the quantities $(t_{xx}, \dots, t_{xy})$ or $(a, \dots, \frac{1}{2}h)$ or $(A', \dots, \frac{1}{2}H')$ is that for a contravariant tensor.

It has now been shown that the stress-strain-velocity relations (9.6) are admissible as the description of the flow properties of an incompressible fluid from the stand-points that they are invariant under a transformation from one rectangular, Cartesian reference system to another and that they lead to a dissipation function which is a function of the flow invariants. In the next section it will be shown that equations (9.6) represent the most general form which can be taken by the stress-strain-velocity relations for an incompressible, visco-inelastic fluid.

11. THE GENERAL STRESS-STRAIN-VELOCITY RELATIONS

In this section, we shall prove that any stress-strain-velocity relations which are suitable for describing the properties of an incompressible, visco-inelastic fluid must have the form of equations (9.6) or be capable of being written in this form.

If the axes (X, Y, Z) of the flow quadrics, represented by equations (2.9) or (2.17), are taken as the axes of reference, then the stress-strain-velocity relations (9.6), in the neighbourhood of the point to which these flow quadrics apply, take the form

$$\left. \begin{aligned} t_{XX} &= 2\Theta U_1 + 2\Psi U_1^2 + p, \\ t_{YY} &= 2\Theta U_2 + 2\Psi U_2^2 + p, \\ t_{ZZ} &= 2\Theta U_3 + 2\Psi U_3^2 + p \\ \text{and} \quad t_{YZ} &= t_{ZX} = t_{XY} = 0. \end{aligned} \right\} \quad (11.1)$$

Conversely, if the stress-strain-velocity relations take this form in the axial system (X, Y, Z) , they will take the form (9.6) in the axial system (x, y, z) .

Since the fluid is isotropic in its state of rest, the stress-strain-velocity relations in the axial system (X, Y, Z) must be symmetrical with respect to a cyclic rotation of the co-ordinates (X, Y, Z) and since the fluid is visco-inelastic the principal stress components must be functions of U_1, U_2 and U_3 only. Thus, the most general form for the stress-strain-velocity relationships in the co-ordinate system (X, Y, Z) is

$$\left. \begin{aligned} t_{XX} &= F(U_1, U_2, U_3) + p, \\ t_{YY} &= F(U_2, U_3, U_1) + p, \\ t_{ZZ} &= F(U_3, U_1, U_2) + p \\ \text{and} \quad t_{YZ} &= t_{ZX} = t_{XY} = 0, \end{aligned} \right\} \quad (11.2)$$

where F is an arbitrary function.

Two of the relations (4.8) can be used to eliminate U_2 and U_3 from the first of equations (11.2), U_3 and U_1 from the second of equations (11.2) and U_1 and U_2 from the third of equations (11.2). Equations (11.2) then take the form

$$t_{XX} = F'(K_2, K_3, U_1) + p, \text{ etc.} \quad (11.3)$$

Now $F''(K_2, K_3, U_1)$ can be expanded, with any desired degree of accuracy, over any desired range of values of U_1 , as a polynomial in U_1 , the coefficients in which are functions of the flow invariants K_2 and K_3 only. From (4.8), it can readily be seen that

$$U_1^3 = K_3 - U_1 K_2.$$

Employing this expression to substitute for U_1^3 in the polynomial expansion of $F''(K_2, K_3, U_1)$, we obtain

$$F''(K_2, K_3, U_1) = 2\Theta U_1 + 2\Psi U_1^2, \quad (11.4)$$

where Θ and Ψ are functions of K_2 and K_3 only. Strictly, the right-hand side of (11.4) contains, in general, a further term which is a function of K_2 and K_3 only, but this may be incorporated with p in (11.3).

In a similar manner, analogous expressions for $F''(K_2, K_3, U_2)$ and $F''(K_2, K_3, U_3)$ can be found. Introducing these into equations (11.3), we obtain equations (11.1), which are therefore the most general stress-strain-velocity relations that can be used to describe the flow properties of a fluid. These are, of course, referred to the axes of flow as reference co-ordinates. Referred to the general rectangular, Cartesian co-ordinate system (x, y, z) , they take the form (9.6).

Reiner (1945) obtained stress-strain-velocity relations similar to (9.6) for a general, compressible fluid, in order to explain the phenomenon of dilatancy. In his equations p is replaced by an arbitrary function of the strain-velocity invariants K_1 , K_2 and K_3 , and Θ and Ψ are also functions of these three strain-velocity invariants. It does not appear that the non-vanishing of Ψ is in any way essential to dilatancy.

12. THE EULERIAN EQUATIONS OF MOTION

The Eulerian equations of motion for a fluid may be written (see, for example, Lamb (1924, §328)) in terms of the stress components in the co-ordinate system (x, y, z) as

$$\rho \frac{Du}{Dt} = \rho X + \frac{\partial t_{xx}}{\partial x} + \frac{\partial t_{xy}}{\partial y} + \frac{\partial t_{xz}}{\partial z}, \text{ etc.}, \quad (12.1)$$

where ρ is the density of the fluid and X , Y , Z are the components parallel to the axes x , y and z respectively of the body force per unit mass of the fluid acting at the point (x, y, z) . The operator D/Dt has the meaning expressed by

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u \frac{\partial}{\partial x} + v \frac{\partial}{\partial y} + w \frac{\partial}{\partial z}. \quad (12.2)$$

Substituting in equations (12.1) the general expressions (9.6) for the stress components, we obtain the equations of motion for an incompressible, non-Newtonian fluid in terms of the velocity components u , v and w .

13. THE BOUNDARY CONDITIONS

Let us suppose that surface tractions, of which the components parallel to the axes x , y and z are X_n , Y_n and Z_n , respectively per unit area of the boundary, are applied to the boundary surface of the fluid at the point (x, y, z) on it. X_n , Y_n and Z_n are

functions of the position (x, y, z) on the boundary and of the time t . At each instant, the components parallel to x , y and z of the forces, due to the stress, at the boundary of the liquid must be in equilibrium with those due to the applied surface tractions. We thus obtain, the three boundary conditions (Lamb 1924, §§ 325 and 327)

$$t_{xx} \cos(x, \nu) + t_{xy} \cos(y, \nu) + t_{xz} \cos(z, \nu) = X_\nu, \text{ etc.} \quad (13.1)$$

where (x, ν) , (y, ν) and (z, ν) are the angles between the normal ν to the surface at the point (x, y, z) and the x , y and z axes respectively.

Again we can substitute in (13.1) the expressions for the stress components given in equations (9.6) and so obtain the boundary conditions in terms of the components u , v and w of the velocity.

As in classical hydrodynamical theory, the boundary conditions may not be given in the form of applied surface tractions, but as specified values of the velocity components u , v and w over the boundary. Again, the boundary conditions may be of the mixed type, in which specified values of the surface tractions are given over part of the boundary surface and specified values of the velocity components u , v and w over the remainder of the boundary.

C. PROBLEMS INVOLVING LAMINAR FLOW

14. INTRODUCTORY REMARKS

It can readily be seen that for laminar flow of the xz -planes of the fluid parallel to the x -axis,

$$u = f(y), \quad v = w = 0.$$

Equations (2.5) and (2.10) yield

$$a = b = c = f = g = 0 \quad \text{and} \quad h = u_y \quad (14.1)$$

$$\text{and} \quad A' = B' = \frac{1}{2}u_y^2, \quad C' = 0, \quad F' = G' = H' = 0. \quad (14.2)$$

Substituting from (14.1) and (14.2) in (9.6), we obtain

$$t_{xx} = t_{yy} = \frac{1}{2}\Psi u_y^2 + p, \quad t_{zz} = p, \quad t_{yz} = t_{zx} = 0 \quad \text{and} \quad t_{xy} = \Theta u_y. \quad (14.3)$$

Thus, apart from an arbitrary hydrostatic pressure, the stress system associated with laminar flow consists of a tangential component and normal components t_{xx} and t_{yy} . These normal components vanish for a Newtonian fluid and indeed for any fluid for which $\Psi = 0$ in equations (9.6).

In §§ 15 and 16, we shall consider in greater detail certain problems of laminar flow which are of practical interest.

15. TORSIONAL MOTION OF A CYLINDRICAL MASS OF FLUID

In this section the torsional motion of a cylindrical mass of incompressible fluid about its axis will be considered. Let us assume that the radius and length of this mass of fluid are a and l respectively. Let us assume that each point of the fluid

moves in a circular path about the axis of the cylinder with a speed which is proportional to its distance r from the axis and its distance z from one end of the cylinder.

Let us take as axes of reference, a rectangular, Cartesian co-ordinate system (x, y, z) , which has its z -axis coincident with the axis of the cylinder and its x - and y -axes in the plane of one end of the cylinder. Then the components u, v and w of the velocity of a point of the fluid, which is at (x, y, z) , parallel to the axes x, y and z of the rectangular, Cartesian co-ordinate system, are given by

$$u = -\psi yz, \quad v = \psi xz \quad \text{and} \quad w = 0, \quad (15.1)$$

$$\text{where} \quad r^2 = x^2 + y^2 \quad (15.2)$$

and ψ is a constant. From equations (15.1) and (2.5), we see that for this motion of the fluid,

$$a = 0, \quad b = 0, \quad c = 0, \quad f = \psi x, \quad g = -\psi y \quad \text{and} \quad h = 0. \quad (15.3)$$

Again, from equations (15.3) and (2.10), we see that

$$\left. \begin{aligned} A' &= \frac{1}{4}\psi^2 y^2, & B' &= \frac{1}{4}\psi^2 x^2, & C' &= \frac{1}{4}\psi^2 r^2, & F' &= 0, \\ G' &= 0 & \text{and} & & H' &= -\frac{1}{2}\psi^2 xy. \end{aligned} \right\} \quad (15.4)$$

Further, employing the relations (15.3) in (4.8), we obtain

$$K_2 = -\frac{1}{4}\psi^2 r^2 \quad \text{and} \quad K_3 = 0. \quad (15.5)$$

Also, it is seen that the relation (5.2), which must be valid for an incompressible fluid, is automatically satisfied.

If the stress-strain-velocity relationships take the form (9.6), we can find the stress components at the point (x, y, z) by introducing the relations (15.3), (15.4) and (15.5) into (9.6). We obtain

$$\left. \begin{aligned} t_{xx} &= 2\Psi(\frac{1}{4}\psi^2 y^2) + p, \\ t_{yy} &= 2\Psi(\frac{1}{4}\psi^2 x^2) + p, \\ t_{zz} &= 2\Psi(\frac{1}{4}\psi^2 r^2) + p, \\ t_{yx} &= \Theta(\psi x), \\ t_{xz} &= \Theta(-\psi y) \\ t_{xy} &= \Psi(-\frac{1}{2}\psi^2 xy), \end{aligned} \right\} \quad (15.6)$$

and

where Θ and Ψ are now functions of K_2 only, K_3 being given by (15.5).

Introducing these expressions for the stress components into the equations of motion (12.1), together with the formulae (15.1) for u, v and w , we obtain

$$\left. \begin{aligned} -\rho\psi^2 xz &= \rho X + \frac{\partial p}{\partial x} - \frac{1}{2}\psi^2 x\Psi, \\ -\rho\psi^2 yz &= \rho Y + \frac{\partial p}{\partial y} - \frac{1}{2}\psi^2 y\Psi, \\ 0 &= \rho Z + \frac{\partial p}{\partial z}. \end{aligned} \right\} \quad (15.7)$$

and

Let us assume that ρz^2 is small compared with Ψ at all points of the fluid mass, so that the components of the centrifugal force $-\rho\psi^2xz^2$ and $-\rho\psi^2yz^2$ in equations (15.7) can be neglected. If, further, the applied body forces are zero, then equations (15.7) become

$$\frac{\partial p}{\partial x} = \frac{1}{2}\psi^2x\Psi, \quad \frac{\partial p}{\partial y} = \frac{1}{2}\psi^2y\Psi \quad \text{and} \quad \frac{\partial p}{\partial z} = 0. \quad (15.8)$$

It is readily seen that these equations are compatible and lead to the following equation for p :

$$\frac{\partial p}{\partial r} = \frac{1}{2}\psi^2r\Psi. \quad (15.9)$$

Thus, the state of motion described by equations (15.1) can be supported by surface tractions alone.

Let us take at each point of the fluid a rectangular, Cartesian co-ordinate system (r, θ, z) , the axes of which are parallel to the radial, azimuthal and axial directions at that point. Then, the orientations of the axes (r, θ, z) with respect to the axes (x, y, z) are given by the scheme

$$\begin{array}{c} r \quad \theta \quad z \\ \begin{array}{c|ccc} x & x/r & -y/r & 0 \\ y & y/r & x/r & 0 \\ z & 0 & 0 & 1 \end{array} \end{array}$$

Therefore, the components of stress $t_{rr}, t_{\theta\theta}, \dots, t_{r\theta}$ in the axial system (r, θ, z) are given by

$$\left. \begin{aligned} t_{rr} &= \frac{x^2}{r^2} t_{xx} + \frac{y^2}{r^2} t_{yy} + \frac{2xy}{r^2} t_{xy}, \\ t_{\theta\theta} &= \frac{y^2}{r^2} t_{xx} + \frac{x^2}{r^2} t_{yy} - \frac{2xy}{r^2} t_{xy}, \\ t_{zz} &= t_{zz}, \\ t_{\theta z} &= \frac{x}{r} t_{yz} - \frac{y}{r} t_{zx}, \\ t_{zr} &= \frac{y}{r} t_{yz} + \frac{x}{r} t_{zx}, \\ \text{and} \quad t_{r\theta} &= -\frac{xy}{r^2} t_{xx} + \frac{xy}{r^2} t_{yy} + \frac{1}{r^2} (x^2 - y^2) t_{xy}. \end{aligned} \right\} \quad (15.10)$$

Introducing into these equations the expressions (15.6) for $t_{xx}, t_{yy}, \dots, t_{xy}$, we obtain

$$\left. \begin{aligned} t_{rr} &= p, \\ t_{\theta\theta} &= \Psi(\frac{1}{2}\psi^2r^2) + p, \\ t_{zz} &= \Psi(\frac{1}{2}\psi^2r^2) + p, \\ t_{\theta z} &= r\psi\Theta \\ \text{and} \quad t_{zr} &= t_{r\theta} = 0. \end{aligned} \right\} \quad (15.11)$$

Let us assume that when $r = a$, $t_{rr} = 0$ and hence $p = 0$. This enables us to determine the constant of integration in the integral of equation (15.9), giving

$$p = \frac{1}{2}\psi^2 \int_a^r r\Upsilon' dr. \quad (15.12)$$

Now, the surface tractions which must act on the plane ends and on the curved surface of the mass of fluid to maintain the state of motion described by equations (15.1) are given by equations (13.1) and, for the particular problem considered here, could be calculated by introducing the expressions (15.6) for t_{xx} , t_{yy} , ... and writing

$$\cos(x, \nu) = \cos(y, \nu) = 0 \quad \text{and} \quad \cos(z, \nu) = \pm 1,$$

over the plane ends of the cylinder, and

$$\cos(x, \nu) = x/r, \quad \cos(y, \nu) = y/r \quad \text{and} \quad \cos(z, \nu) = 0,$$

over the curved surface of the cylinder. However, it is simpler to calculate directly the radial, azimuthal and longitudinal components, R' , Θ' and Z' respectively, directly by noting that over the curved surface

$$R' = t_{rr}, \quad \Theta' = t_{\theta r} \quad \text{and} \quad Z' = t_{zr} \quad (15.13)$$

and over the plane ends

$$R' = t_{rz}, \quad \Theta' = t_{\theta z} \quad \text{and} \quad Z' = t_{zz}. \quad (15.14)$$

Substituting in (15.13) and (15.14) the expressions for t_{rr} , $t_{\theta\theta}$, ... given in equations (15.11), where p is given by (15.12), we see that, over the curved surface of the cylinder, the surface tractions vanish and, over the plane ends, they are given by

$$R' = 0, \quad \Theta' = r\psi\Theta \quad \text{and} \quad Z' = \frac{1}{2}\psi^2 r^2 \Upsilon' + \frac{1}{2}\psi^2 \int_a^r r\Upsilon' dr. \quad (15.15)$$

The couple which must be exerted on a plane end of the cylindrical mass of fluid is

$$\int_0^a \Theta' 2\pi r^2 dr = 2\pi\psi \int_0^a r^3 \Theta dr. \quad (15.16)$$

Since Θ is a function of K_2 and K_3 which, for the motion considered, are given by (15.5), the expression (15.16) can readily be calculated if the form of Θ as a function of K_2 and K_3 is known.

It is apparent from (15.15) that, in general, to produce the motion described by (15.1) it is necessary to exert, in addition to the couple, a normal surface traction. The presence of the terms $2\Psi A'$, ..., $\Psi F'$, ... on the right-hand sides of the stress-strain-velocity relations (9.6) does not alter the value of the couple (15.16) and the presence of the terms $2\Theta a$, ..., Θf , ... does not affect the value of normal surface traction Z' given by (15.15). Therefore, experiments in which the dependence of the couple (15.16) on ψ is measured can only yield information on the form of Θ for the material and, since $K_3 = 0$ for the motion considered, only on its dependence on

K_2 when $K_2 = 0$. Again, experiments in which Z' is measured can yield information only on the form of Ψ as a function of K_2 , when $K_2 = 0$.

In the simplest case of equations (9.6), for which $\Psi \neq 0$, Θ and Ψ are both constants. Then the normal surface tractions Z' , which must be applied to the plane ends of the cylindrical mass of fluid, are given, from (15.15), by

$$Z' = \frac{1}{4}\Psi\psi^2(3r^2 - a^2) \quad (15.17)$$

and the couple which must be exerted is given by (15.16) as

$$\frac{1}{2}\pi\psi\Theta a^4. \quad (15.18)$$

It is seen from (15.17) that Z' changes sign when $r = a/\sqrt{3}$, and is positive or negative when $r = 0$ accordingly as Ψ is negative or positive.

16. FLOW BETWEEN ROTATING INFINITE CYLINDERS

We shall now consider the motion of an incompressible fluid, whose stress-strain-velocity relationships take the form (9.6), between two infinite, coaxial cylinders of radii a_1 and a_2 respectively ($a_2 > a_1$), when the angular velocity of the outer cylinder is Ω_2 and that of the inner cylinder is Ω_1 . We shall assume that each point of the fluid moves in a plane perpendicular to the common axis of the cylinders and in a circular orbit about this axis.

If the angular velocity of the fluid at a point distant r from the axis of the cylinders is Ω , then

$$\Omega = \Omega_1, \text{ when } r = a_1, \text{ and } \Omega = \Omega_2, \text{ when } r = a_2. \quad (16.1)$$

It is noted that for the state of motion described, Ω is a function of r only. Let us take as axes of reference a rectangular, Cartesian co-ordinate system (x, y, z) , the z -axis of which coincides with the axis of the cylinders. Then, if u, v and w are the components of velocity of the point (x, y, z) of the fluid parallel to x, y and z respectively, we have

$$u = -y\Omega, \quad v = x\Omega \quad \text{and} \quad w = 0. \quad (16.2)$$

Introducing these expressions for u, v and w into (2.5) and noting that $r^2 = x^2 + y^2$, we obtain

$$\left. \begin{aligned} a &= -\frac{xy}{r}\Omega_r, & b &= \frac{xy}{r}\Omega_r, & c &= 0, \\ f &= 0, & g &= 0 & \text{and} & h = \frac{1}{r}(x^2 - y^2)\Omega_r. \end{aligned} \right\} \quad (16.3)$$

Substituting these expressions in (2.10), we obtain

$$A' = \frac{1}{4}r^2\Omega_r^2, \quad B' = \frac{1}{4}r^2\Omega_r^2, \quad C' = 0, \quad F' = 0, \quad G' = 0 \quad \text{and} \quad H' = 0. \quad (16.4)$$

It is readily seen that the relation (5.2), which must be obeyed for any motion of an incompressible fluid, is automatically satisfied by (16.3) and hence for the motion described by (16.2).

Substituting in (4.8), from (16.3), we see that for this motion of the fluid

$$K_1 = -\frac{1}{4}r^2\Omega_r^2 \quad \text{and} \quad K_2 = 0. \quad (16.5)$$

Now, let us consider the case when the stress-strain-velocity relations for the material take the form (9.6). For the motion considered these become

$$\left. \begin{aligned} t_{xx} &= -2\Theta \frac{xy}{r} \Omega_r + 2\Psi \frac{1}{4}r^2\Omega_r^2 + p, \\ t_{yy} &= 2\Theta \frac{xy}{r} \Omega_r + 2\Psi \frac{1}{4}r^2\Omega_r^2 + p, \\ t_{zz} &= p, \\ t_{yz} &= t_{zx} = 0 \\ \text{and} \quad t_{xy} &= \Theta \frac{1}{r} (x^2 - y^2) \Omega_r. \end{aligned} \right\} \quad (16.6)$$

The components of stress $t_{rr}, t_{\theta\theta}, \dots, t_{r\theta}$, defined as in §15, can be calculated by combining equations (16.6) with (15.10). We obtain

$$\left. \begin{aligned} t_{rr} &= t_{\theta\theta} = \frac{1}{2}\Psi r^2\Omega_r^2 + p, \quad t_{zz} = p, \\ t_{\theta z} &= t_{zr} = 0 \quad \text{and} \quad t_{r\theta} = \Theta r \Omega_r. \end{aligned} \right\} \quad (16.7)$$

Substituting the expressions (16.7) and (16.2) in the equations of motion (12.1), we obtain, when the body forces are zero (involving neglect of the gravitational forces on the fluid) so that $X = Y = Z = 0$,

$$\left. \begin{aligned} -\rho x \Omega^2 &= \frac{\partial p}{\partial x} - \frac{4}{r} \Theta y \Omega_r - y r \frac{\partial}{\partial r} \left(\Theta \frac{1}{r} \Omega_r \right) + \frac{\partial}{\partial x} \left(\frac{1}{2} \Psi r^2 \Omega_r^2 \right), \\ -\rho y \Omega^2 &= \frac{\partial p}{\partial y} + \frac{4}{r} \Theta x \Omega_r + x r \frac{\partial}{\partial r} \left(\Theta \frac{1}{r} \Omega_r \right) + \frac{\partial}{\partial y} \left(\frac{1}{2} \Psi r^2 \Omega_r^2 \right), \\ \text{and} \quad 0 &= \frac{\partial p}{\partial z}. \end{aligned} \right\} \quad (16.8)$$

Since

$$\frac{\partial p}{\partial r} = \frac{x}{r} \frac{\partial p}{\partial x} + \frac{y}{r} \frac{\partial p}{\partial y} \quad (16.9)$$

and

$$\frac{\partial p}{\partial \theta} = -y \frac{\partial p}{\partial x} + x \frac{\partial p}{\partial y},$$

we obtain, from (16.8),

$$\left. \begin{aligned} \frac{\partial p}{\partial r} &= -\rho r \Omega^2 - \frac{\partial}{\partial r} \left(\frac{1}{2} \Psi r^2 \Omega_r^2 \right) \\ \text{and} \quad \frac{\partial p}{\partial \theta} &= -4r^2 \left(\Theta \frac{1}{r} \Omega_r \right) - r^2 \frac{\partial}{\partial r} \left(\Theta \frac{1}{r} \Omega_r \right). \end{aligned} \right\} \quad (16.10)$$

If p is independent of θ , as it must be for the cylindrically symmetrical state of flow we have assumed, $\partial p / \partial \theta = 0$ and the second of equations (16.10) yields

$$\Theta \frac{1}{r} \Omega_r = \frac{C}{r^4}, \quad (16.11)$$

where C is a constant of integration.

It can readily be seen, by direct substitution in (16.8), that if $\Theta \frac{1}{r} \Omega_r$ is given by (16.11), equations (16.8) are compatible. If the form of Θ as a function of K_s and K_z and hence, from (16.5), of $-\frac{1}{2}r^2\Omega_r^2$, is known, equation (16.11) can be used to obtain Ω as a function of r . The integration involved introduces a further constant of integration and this, together with C in (16.11), can be obtained by employing the two boundary conditions (16.1). It is clear that the radial distribution of the angular velocity is unaffected by the presence in the stress-strain-velocity relations (9.6) of the terms containing Ψ . However, from the first of equations (16.10), it is seen that

$$p = - \int \rho r \Omega^2 dr - \frac{1}{2} \Psi r^2 \Omega_r^2 + C', \quad (16.12)$$

where C' is a constant of integration.

Introducing expression (16.12) for p , the stress components (16.7) for the state of motion considered become

$$\left. \begin{aligned} t_{rr} &= t_{\theta\theta} = - \int \rho r \Omega^2 dr + C', \\ t_{zz} &= - \int \rho r \Omega^2 dr - \frac{1}{2} \Psi r^2 \Omega_r^2 + C', \\ t_{\theta z} &= t_{zr} = 0 \\ t_{r\theta} &= \Theta r \Omega_r. \end{aligned} \right\} \quad (16.13)$$

and

It is seen that the presence of the terms containing Ψ in the stress-strain-velocity relations (9.6) modifies the expressions for the stress components to the extent of the term $-\frac{1}{2}\Psi r^2\Omega_r^2$ in the expression for t_{zz} .

If the form of the stress-strain-velocity relations is known, then (16.13) can be used to determine the necessary surface tractions that must be applied to the mass of fluid to produce the state of motion described by (16.2).

If the angular velocity Ω is sufficiently small then the terms $-\int \rho r \Omega^2 dr$ in (16.13) can be neglected. If the length of the cylindrical mass of fluid is finite, then the system of external forces which must be applied to maintain the state of motion considered consists of (i) azimuthal surface tractions acting over the inner and outer curved surfaces of the fluid mass of amounts C/a_1^2 and C/a_2^2 respectively, (ii) a normal surface traction acting over the plane ends of the fluid mass of amount $-\frac{1}{2}\Psi C^2/\Theta^2 r^4$, and (iii) an arbitrary uniform normal surface traction C' , acting over the whole of the surface of the fluid.

The surface tractions (i) imply that in order to produce in the fluid the state of motion under discussion, equal and oppositely directed couples of magnitude $2\pi C$ must be applied to the confining cylinders per unit length. It is noted too that the surface traction (ii) vanishes when $\Psi = 0$, for the state of motion considered.

For the particular case, when Θ is a constant, we find, from (16.11) and (16.1), that

$$C = 2\Theta(\Omega_1 - \Omega_2) \frac{a_1^2 a_2^2}{a_1^2 - a_2^2}, \quad (16.14)$$

so that the surface traction (ii) becomes

$$-2\Psi(\Omega_1 - \Omega_2)^2 \left(\frac{a_1^2 a_2^2}{a_1^2 - a_2^2} \right)^2 \frac{1}{r^4}. \quad (16.15)$$

If Ψ is constant, this is positive or negative depending on the sign of Ψ . If the surface traction (16.15) is not applied, the surface of the fluid will have a tendency to rise or fall at the surface of the inner cylinder accordingly as Ψ is positive or negative. In either case, the effect will be greatest at the inner confining cylinder.

17. GENERAL REMARKS

A fluid is generally recognized as non-Newtonian on the basis of viscosimetric experiments. For a Newtonian fluid in a steady state of laminar flow, a linear relation obtains between the shearing stress and rate of shear. It is generally assumed that if such a relation is obtained experimentally, the fluid under investigation is Newtonian and that the whole of the classical hydrodynamic theory for viscous fluids is applicable. It is seen, from the results of §§ 15 and 16, that this is by no means correct. Fluids, which appear Newtonian on the basis of experiments involving steady-state laminar flow, may, from the stand-point of the phenomenological theory, be non-Newtonian and distinguishable from Newtonian fluids by other steady-state experiments in which the flow is not laminar.

It should be remarked that any visco-elastic material, which is fluid-like in its ability to be continuously deformed, cannot be distinguished from a visco-inelastic fluid solely by means of steady-state experiments, in which the flow is laminar. For example, suppose the fundamental stress-strain-velocity relations for the material involve time derivatives of the stress components. For a steady state of flow, these vanish and the stress-strain-velocity relations are indistinguishable from those describing a true fluid.

It may well be that the theory formulated in the present paper may have as an important field of application the correlation of the steady-state laminar flow properties of such visco-elastic materials.

Effects similar to those predicted from the theory of §§ 15 and 16 have been described in a number of fluids by Weissenberg (1947). They are interpreted by him as arising from the fact that the fluids concerned have highly-elastic as well as viscous properties. It does not, however, appear that this explanation can be correct, from a phenomenological point-of-view, since, in the experiments, the fluids are in a steady-state of laminar flow. In the theory presented here, these phenomena appear to arise from the non-vanishing of Ψ in the stress-strain-velocity relations. From a phenomenological point-of-view, this does not imply that the fluid is visco-elastic. However, it may be that the microscopic or molecular features of a fluid, which lead to a non-zero value for Ψ , also result in the fluid having visco-elastic properties.

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A theory of the yielding and plastic flow of anisotropic metals

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A theory is suggested which describes, on a macroscopic scale, the yielding and plastic flow of an anisotropic metal. The type of anisotropy considered is that resulting from preferred orientation. A yield criterion is postulated on general grounds which is similar in form to the Huber-Mises criterion for isotropic metals, but which contains six parameters specifying the state of anisotropy. By using von Mises' concept (1928) of a plastic potential, associated relations are then found between the stress and strain-increment tensors. The theory is applied to experiments of Körber & Hoff (1928) on the necking under uniaxial tension of thin strips cut from rolled sheet. It is shown, in full agreement with experimental data, that there are generally two, equally possible, necking directions whose orientation depends on the angle between the strip axis and the rolling direction. As a second example, pure torsion of a thin-walled cylinder is analyzed. With increasing twist anisotropy is developed. In accordance with recent observations by Swift (1947), the theory predicts changes in length of the cylinder. The theory is also applied to determine the earing positions in cups deep-drawn from rolled sheet.

1. INTRODUCTION

The macroscopic yielding and plastic straining of isotropic ductile metals has been described by theories which may be regarded as essentially satisfactory. The well-known Huber-Mises criterion for determining the elastic limit under combined stresses of metals which deform homogeneously, for example, copper, aluminium, nickel, has been confirmed by many experiments over the last twenty years. There are one or two exceptions, notably annealed mild steel which softens after yielding. The specimen is traversed by Lüders' bands and the deformation is non-uniform. In such circumstances the maximum shear-stress criterion of Coulomb or Tresca is found to be a better approximation than that of Huber-Mises. This is hardly

surprising since each Lüders' band is a region where the deformation is a simple shear. For metals obeying the Huber-Mises law of yielding, the relation between the plastic strain-increment and the applied combined stress is given by the Lévy-Mises equations. Strain-hardening can also be taken into account in a relatively simple way which is fairly satisfactory for biaxial stress systems and limited strain ranges.

With increasing strain, however, a preferred orientation of crystal planes and directions gradually develops, and the individual crystals become elongated to form a characteristic fibrous texture in the direction of the most severe tensile strain. In this way an originally isotropic metal becomes anisotropic in respect of many physical properties. It is well known that the fibre texture produced in the technological forming processes, rolling, drawing, and extrusion, is sometimes the cause of undesirable properties in the final product. The most familiar example is perhaps that of the 'earring' of cups deep-drawn from rolled sheet. After severe cold-rolling the yield stress may be as much as 10 % higher in directions across the fibre than it is along the fibre (Cook 1937). Ductility shows even more pronounced directional properties. Such anisotropy can only be removed with difficulty by careful heat treatment. More often the metallurgist must be content with a compromise in which a final preferred orientation of allowable proportions is retained. Preferred orientation is not the only cause of anisotropic plastic properties: laminar inclusions and cavities occasionally produce similar effects. Residual or internal stresses are another cause. The present theory is, however, probably valid only when the anisotropy is due to preferred orientation.

Anisotropy, then, is not to be considered a phenomenon of rather rare occurrence. It is difficult to avoid in metal working and is invariably developed by any severe strain. Whenever it is present the theories of plastic flow for isotropic metals are only valid to a first approximation. This approximation is good enough for many purposes, but there are also many phenomena for which these theories fail to account. The object of the present paper is to formulate a theory capable of describing the macroscopic behaviour of anisotropic metals. Such a theory must be constructed on *a priori* reasoning since no suitable data are as yet available to check individual assumptions. It will be shown finally, however, that the theory is, as a whole, in close agreement with certain experimental observations.

2. THE PLASTIC POTENTIAL

In 1928, von Mises, in a brilliant paper on the plastic distortion of crystals, introduced the fruitful concept of a plastic potential. A detailed account has been given by Geiringer (1937). This concept will now be explained as it is basic in constructing the new theory.

Suppose the criterion of yielding under combined stresses is

$$f(\sigma_{ij}) = \text{constant}, \quad (1)$$

where f is regarded as a function of the components of the stress tensor. The function f will also involve certain parameters characterizing the current state of the material. Von Mises suggested that the relation between the stress tensor σ_{ij} and the natural strain-increment tensor $d\epsilon_{ij}$ which should be used in conjunction with this yield criterion is simply

$$d\epsilon_{ij} = \frac{\partial f}{\partial \sigma_{ij}} d\lambda. \quad (2)$$

Here $d\lambda$ is a positive scalar factor of proportionality. When carrying out the partial differentiation it is important to remember that σ_{ij} , σ_{ji} ($i \neq j$) must be counted as different for the purposes of tensor analysis. If the metal is isotropic f will not depend on the choice of axes, and equation (2) is then a true tensor relation. When the metal is anisotropic the form of f depends, as we shall see, on the choice of axes of reference. The function f is called the plastic potential.

Let us examine what validity von Mises' idea has in relation to the known plastic properties of single crystals and quasi-isotropic polycrystals. The Huber-Mises criterion of yielding for the latter is

$$2f(\sigma_{ij}) \equiv (\sigma_{xx} - \sigma_{yy})^2 + (\sigma_{yy} - \sigma_{zz})^2 + (\sigma_{zz} - \sigma_{xx})^2 + 6(\sigma_{xy}^2 + \sigma_{yz}^2 + \sigma_{zx}^2) = 2Y^2, \quad (3)$$

where Y is the yield stress of a bar in uniaxial tension. Regarding the nine stress components as distinct independent variables, we find

$$\frac{\partial f}{\partial \sigma_{xx}} = (2\sigma_{xx} - \sigma_{yy} - \sigma_{zz}), \quad \frac{\partial f}{\partial \sigma_{yy}} = \frac{\partial f}{\partial \sigma_{zz}} = 3\sigma_{yz}, \quad \text{etc.}$$

Now the Lévy-Mises stress-strain relations are

$$d\epsilon_{xx} = d\lambda(2\sigma_{xx} - \sigma_{yy} - \sigma_{zz}), \quad d\epsilon_{yz} = 3d\lambda\sigma_{yz}, \quad \text{etc.}, \quad (4)$$

where $d\epsilon_{xx}$, $d\epsilon_{yz}$, etc. are components of the natural strain-increment tensor. Hence equations (4) can be written in the form of equation (2).

Consider next a metal single-crystal which is generally accepted as yielding when the shear stress, acting over a certain crystal plane in a certain specific direction, reaches a limiting value. If axes are chosen so that the shear stress is σ_{yz} , then the criterion of yielding is $f(\sigma_{ij}) \equiv \sigma_{yz} = \text{constant}$. From equation (2) we find that the strain-increment tensor has only two non-vanishing components viz. $d\epsilon_{yz}$ and $d\epsilon_{zy}$, which are of course equal. This represents a shear in the yz plane in the direction of the shear stress, which is what is actually observed.

In annealed mild steel yielding begins when the maximum shear stress reaches a limiting value. Proceeding as with the single crystal, equation (2) implies that the ensuing strain is a shear in the direction of the maximum shear stress. This is just what happens within a Lüders' band. Prestrained mild steel, however, is like most ductile metals in following both the Huber-Mises and Lévy-Mises laws (Taylor & Quinney 1931).

The success of the plastic potential in these examples gives confidence in applying it to anisotropic polycrystalline metals. Von Mises himself was concerned with

single crystals. However, the idea seems of wider validity, for in spite of its apparent artificiality it can be given a physical interpretation. This, too, is due to von Mises. Consider the work $\sigma_{ij}d\epsilon_{ij}$ done on a small element in deforming it through a given plastic strain-increment $d\epsilon_{ij}$. Suppose we arbitrarily vary σ_{ij} , subject only to the restriction imposed by the yield criterion $f(\sigma_{ij}) = \text{constant}$. Then for given $d\epsilon_{ij}$ the work done has a stationary value when σ_{ij} assumes its actual value given by equation (2). Stationary values of $\sigma_{ij}d\epsilon_{ij}$, subject to $f(\sigma_{ij}) = \text{constant}$, are given, in the usual way, by

$$\frac{\partial}{\partial \sigma_{ij}}(\sigma_{ij}d\epsilon_{ij} - f d\lambda) = 0,$$

where $d\lambda$ is an undetermined constant multiplier. This leads immediately to equation (2) and the statement is proved. In the special case when f is the Huber-Mises expression the work done has a maximum value (Hill, Lee & Tupper 1947), but this may not be true in general. It is true for the yield criterion proposed in § 3, except possibly when one of F , G , H is negative.

3. A YIELD CRITERION FOR ANISOTROPIC METALS

It is assumed that the anisotropy has three mutually orthogonal planes of symmetry at every point. The three planes of symmetry meet in three orthogonal directions which may be called the principal axes of anisotropy. These axes can, and frequently will, vary in direction at any moment from point to point of the bulk metal. For example, if anisotropy is developed through the severe uniform expansion of a hollow cylinder by internal pressure, the principal axes of anisotropy can be expected to lie in the radial, circumferential and longitudinal directions. An example of uniformly directional anisotropy would be that in a bar cut from the central part of a cold-rolled sheet; the principal axes would lie in the direction of rolling, transversely in the plane of the sheet, and normal to this plane. Again, the principal axes in a given element can vary relatively to the element itself as deformation continues, for example, in simple torsion of a hollow cylinder.

Let us fix our attention on a given element in a certain state of anisotropy and choose the principal axes of anisotropy as Cartesian axes of reference. By analogy with the Huber-Mises yield criterion for isotropic metal it is natural to select some homogeneous quadratic in the stresses to represent the plastic potential. This would imply that the yield stress in tension for any direction is the same as that in compression, i.e. the absence of a Bauschinger effect. Now cold work does generally give rise to a Bauschinger effect, just as it produces a preferred orientation and fibre texture. The former can be removed by mild annealing, but the latter remains. Hence it is perfectly possible, both in principle and in practice, to have an anisotropic metal with no Bauschinger effect. The Bauschinger effect will be ignored in the present analysis; it will not be difficult to take account of it when experiment shows such a refinement in the theory to be desirable. We can, then, safely choose a homogeneous quadratic for the plastic potential. Furthermore, in view of the symmetry

assumption, terms in which any one shear stress occurs linearly must be rejected. If it be also assumed that the superposition of hydrostatic pressure does not influence yielding, the plastic potential or yield criterion takes the form

$$2f = F(\sigma_{yy} - \sigma_{zz})^2 + G(\sigma_{zz} - \sigma_{xx})^2 + H(\sigma_{xx} - \sigma_{yy})^2 + 2L\sigma_{yz}^2 + 2M\sigma_{zx}^2 + 2N\sigma_{xy}^2 = 1. \quad (5)$$

F, G, H, L, M, N are constants characteristic of the current state of anisotropy. The expression for f only has this form when the principal axes of anisotropy are chosen as axes of reference. If other axes of reference are taken, the form changes in a way that can be found by transforming the stress components.

If X, Y, Z are the tensile yield stresses in the principal anisotropic directions, it is easily seen that

$$\left. \begin{aligned} \frac{1}{X^2} &= G + H, & 2F &= \frac{1}{Y^2} + \frac{1}{Z^2} - \frac{1}{X^2}, \\ \frac{1}{Y^2} &= H + F, & 2G &= \frac{1}{Z^2} + \frac{1}{X^2} - \frac{1}{Y^2}, \\ \frac{1}{Z^2} &= F + G, & 2H &= \frac{1}{X^2} + \frac{1}{Y^2} - \frac{1}{Z^2}. \end{aligned} \right\} \quad (6)$$

It is clear that only one of F, G, H can be negative, a situation which, however, is unlikely to occur in practice, since it implies rather large differences between the yield stresses. Also $F > G$ if and only if $X > Y$, etc. These inequalities will be used later when comparing theory and experiment. If R, S, T are the yield stresses in shear with respect to the principal axes of anisotropy, then

$$2L = \frac{1}{R^2}, \quad 2M = \frac{1}{S^2}, \quad 2N = \frac{1}{T^2}. \quad (7)$$

L, M, N are thus essentially positive.

To describe fully the state of anisotropy in an element the six independent yield stresses, X, Y, Z, R, S, T need to be given. They must be considered as dependent on the strain-history of the material and so varying with strain. For present purposes it is not necessary to specify the state of anisotropy more closely than this. No attempt will be made to examine, for example, how the yield stresses change with increasing distortion, or how they can be quantitatively related to the degree of preferred orientation.

If there is rotational symmetry of the anisotropy in an element about the z axis, then

$$F = G, \quad N = G + 2H. \quad (8)$$

This may be verified by requiring the form of f to remain invariant for arbitrary x, y axes of reference. For complete spherical symmetry, i.e. isotropy, $F = G = H$ and $L = M = N = 3F$. The expression (5) is then identical with (3) when $2F$ is put equal to $1/Y^2$.

It might be asked why f is not taken as the expression for the distortional energy due to shear alone in an anisotropic elastic medium, by analogy with Hencky's

interpretation of the Huber-Mises yield criterion for isotropic materials. There are two objections to this procedure. A hydrostatic pressure generally produces shear strain in an anisotropic elastic material. Hence we cannot take the expression for shear-strain energy as the plastic potential without implying that a superposed hydrostatic pressure influences yielding. Again, the anisotropic shear-strain energy is not independent of elastic constants as is the isotropic shear-strain energy, apart from a multiplying factor. The elastic constants will therefore appear in the expression (2) for the plastic strain-increment. This is of course not physically plausible.

4. RELATIONS BETWEEN STRESS AND STRAIN-INCREMENT FOR ANISOTROPIC METALS

By applying the equation (2) to the yield criterion (5) the following expressions are obtained, relating the components of the strain-increment tensor to the stress components.

$$\left. \begin{aligned} d\epsilon_{xx} &= d\lambda [H(\sigma_{xx} - \sigma_{yy}) + G(\sigma_{xx} - \sigma_{zz})], & d\epsilon_{yz} &= d\lambda L\sigma_{yz}, \\ d\epsilon_{yy} &= d\lambda [F(\sigma_{yy} - \sigma_{zz}) + H(\sigma_{yy} - \sigma_{xx})], & d\epsilon_{zx} &= d\lambda M\sigma_{zx}, \\ d\epsilon_{zz} &= d\lambda [G(\sigma_{zz} - \sigma_{xx}) + F(\sigma_{zz} - \sigma_{yy})], & d\epsilon_{xy} &= d\lambda N\sigma_{xy}. \end{aligned} \right\} \quad (9)$$

It will be noticed that $d\epsilon_{xx} + d\epsilon_{yy} + d\epsilon_{zz} = 0$ identically for all stress systems. This of course is essential in view of the known fact that the volume change associated with plastic strain is negligible. The zero volume change is directly connected with the assumption that yielding is independent of hydrostatic pressure. Either is a consequence of the other for any yield criterion whatever. This can most readily be seen by considering the stationary work interpretation of the plastic potential method. For a superposed hydrostatic pressure does not change the work done in a given strain when the volume change is zero. Thus if we accept, as experimental facts, the zero plastic volume change and the independence of the yield criterion with respect to hydrostatic pressure, then the method of the plastic potential is not only consistent with both but provides a link between them.

When using the above equations it must be remembered that they only have this form when the stresses and strain-increments are referred to the principal axes of anisotropy. Further, the principal axes of stress and strain-increment coincide when the principal stress directions are along the principal axes of anisotropy, but not in general otherwise.

Consider now some simple stress systems for a material with anisotropy uniformly distributed in magnitude and direction. In pure tension X parallel to the principal x axis of anisotropy the incremental strains at a certain stage are

$$d\epsilon_{xx} : d\epsilon_{yy} : d\epsilon_{zz} = (G + H) : -H : -G.$$

The specimen contracts in the transverse directions unless one of G and H is negative, which seems hardly likely to occur. The contraction in the y direction is greater than that in the z direction if $H > G$, i.e. if $Z > Y$. An experimental determination

of the ratio $d\epsilon_{yy}/d\epsilon_{xx}$ would give the value of H/G . Similarly from tension tests in the y, z directions values of $G/F, F/H$ can be found. Apart from the check on the theory in view of the identity $\frac{H}{G} \times \frac{G}{F} \times \frac{F}{H} = 1$, this would allow an alternative way of determining the ratios $X/Y, Y/Z$ of the yield stresses. If the yielding is not particularly sharp, direct measurement of X, Y, Z would be unreliable. Similar experiments can, in principle, be devised to find the shear-stress ratios $R/S, R/T$.

In plane strain, where motion is prevented in the z principal direction of anisotropy, we find by putting $d\epsilon_{zz} = 0$ in equation (9) that

$$\sigma_{zz} = \frac{G\sigma_{xx} + F\sigma_{yy}}{G + F},$$

and thus from equation (5) that

$$\left(\frac{FG + GH + HF}{F + G} \right) (\sigma_{xx} - \sigma_{yy})^2 + 2N\sigma_{xy}^2 = 1. \quad (10)$$

It is easy to show that the tensile yield stresses are equal in any pair of orthogonal directions in the plane, although σ_{zz} is different in the two cases. It can also be shown that the dependence of the tensile yield stress on orientation is such that maxima or minima occur in directions along the anisotropic axes, or in directions making 45° with the axes. If

$$\frac{2(FG + GH + HF)}{N(F + G)} < 1,$$

the yield stress has a minimum in the 45° directions and a maximum in the x and y directions; for the opposite inequality the reverse is true. When the equality holds, the yield stress does not vary with orientation. In view of the identities

$$\frac{2(FG + GH + HF)}{N(F + G)} = \frac{F + 2H}{N} + \frac{F(G - F)}{N(F + G)} = \frac{G + 2H}{N} + \frac{G(F - G)}{N(F + G)},$$

it is clear that when

$$N > F + 2H, \quad G + 2H, \quad \text{then} \quad \frac{2(FG + GH + HF)}{N(F + G)} < 1;$$

$$\text{and when} \quad N < F + 2H, \quad G + 2H, \quad \text{then} \quad \frac{2(FG + GH + HF)}{N(F + G)} > 1.$$

The physical significance of these inequalities will be further exemplified in § 5.

The relations between the components of the strain-increment and stress tensors in a state of plane strain are

$$\left. \begin{aligned} d\epsilon_{xx} + d\epsilon_{yy} &= 0, \\ \frac{d\epsilon_{xx} - d\epsilon_{yy}}{2d\epsilon_{xy}} &= \frac{2(FG + GH + HF)(\sigma_{xx} - \sigma_{yy})}{N(F + G) \cdot 2\sigma_{xy}} \end{aligned} \right\} \quad (11)$$

Hence if ψ is the angle between a principal stress direction and the x axis, and ψ' is the angle between a principal strain-increment direction and the x axis, then

$$\frac{\tan 2\psi}{\tan 2\psi'} = \frac{2(FG + GH + HF)}{N(F + G)}. \quad (12)$$

Hence $\psi = \psi'$ if, and only if, $\psi = 0, \pm \frac{1}{2}\pi, \pm \frac{3}{2}\pi$. Thus the principal axes of stress and strain-increment coincide in the directions in which the tensile yield stress has maximum or minimum values. The set of equations (10) and (11) together with the equilibrium equations, considered in terms of the five dependent variables (three stress components and two incremental displacement components) is hyperbolic. There are only two distinct characteristics: these are the orthogonal directions of maximum shear strain-increment or of zero extension. These, as has been remarked, are not generally the directions of maximum shear stress. The four differential relations holding along the characteristics are found to be analogous to the well-known Hencky relations for an isotropic metal. It is scarcely worth while to include an account of these in the present paper while the theory has not yet been sufficiently tested.

For a thin sheet perpendicular to the Z direction and in a state of plane stress

$$(G+H)\sigma_{xx}^2 - 2H\sigma_{xx}\sigma_{yy} + (H+F)\sigma_{yy}^2 + 2N\sigma_{xy}^2 = 1. \quad (13)$$

The maxima and minima of the yield stress in uniaxial tension occur along the anisotropic axes and in a direction θ with respect to the x axis, where

$$\tan^2 \theta = \frac{N-G-2H}{N-F-2H}. \quad (14)$$

If $N > F+2H, G+2H$, the yield stress has maximum (unequal) values in the x, y directions and minimum (equal) values in the θ directions.* If $N < F+2H, G+2H$, the converse is true. If N is intermediate to $F+2H$ and $G+2H$ there is no real θ satisfying equation (14). The yield stress then has a maximum in the x direction and a minimum in the y direction if $F > G$, and vice versa. The relations between the components of the strain-increment and stress tensors in a state of plane stress are

$$\left. \begin{aligned} \frac{d\epsilon_{xx}}{d\epsilon_{yy}} &= \frac{(G+H)\sigma_{xx} - H\sigma_{yy}}{(F+H)\sigma_{yy} - H\sigma_{xx}}, \\ \frac{d\epsilon_{xx} - d\epsilon_{yy}}{2d\epsilon_{xy}} &= \frac{(G+2H)\sigma_{xx} - (F+2H)\sigma_{yy}}{2N\sigma_{xy}}. \end{aligned} \right\} \quad (15)$$

The principal axes of stress and strain-increment coincide when the principal axes of stress are along the anisotropic axes, and also for special states of stress such that

$$\frac{\sigma_{yy}}{\sigma_{xx}} = \frac{N-G-2H}{N-F-2H}.$$

If the state of stress is a uniaxial tension σ directed at an angle θ with the x axis then

$$\sigma_{xx} = \sigma \cos^2 \theta, \quad \sigma_{yy} = \sigma \sin^2 \theta, \quad \sigma_{xy} = \sigma \sin \theta \cos \theta.$$

The principal axes of stress and strain-increment then coincide when θ has the value given by equation (14). θ is real only when $(N-F-2H)$ and $(N-G-2H)$ have the

* Compare values for 0.1 % proof stress given by Cook (*loc. cit.*, tables I and II).

same sign. The directions for which the principal axes of stress and strain-increment coincide in uniaxial tension are thus those for which the yield stress has maximum and minimum values.

The characteristics for a state of plane stress are in directions satisfying

$$[(G+H)\sigma_{xx}-H\sigma_{yy}]dx^2+2N\sigma_{xy}dxdy+[(F+H)\sigma_{yy}-H\sigma_{xx}]dy^2=0. \quad (16)$$

The characteristics are in the directions of zero extension in the plane of the sheet. They are not generally perpendicular because of the $d\epsilon_{xx}$ strain, nor are they always real. The plane stress problem is thus sometimes hyperbolic and sometimes elliptic, just as in the case of an isotropic metal. The coincidence of the characteristics with the directions of zero extension in both plane strain and plane stress is closely connected with the plastic potential. In these special cases the characteristics can be found for the Cauchy problem in the stresses and the incremental displacements separately, since the full set of equations breaks down into distinct halves. The two pairs of characteristic directions corresponding to the two halves can be shown to be the same if, and only if, the stress-strain equations and the yield criterion are connected on the plastic potential basis.

5. THE NECKING OF STRIP UNDER TENSION

A check on the present theory can be obtained by analyzing the experimental data of Körber & Hoff (1928). These workers carried out tensile tests on strips cut from thin rolled sheet. Now it is well known that a sufficiently thin strip of isotropic metal, pulled in tension, develops a neck making an angle of about 55° with the direction of pull. Körber & Hoff, however, observed that for a strip cut at a definite angle to the rolling direction either of two distinct necking angles occurred apparently at random. Suppose a strip is cut with its length making an angle α with the rolling direction in the original sheet (figure 1*a*). In figure 1*b* the strip is shown with the two equally likely directions of necking.

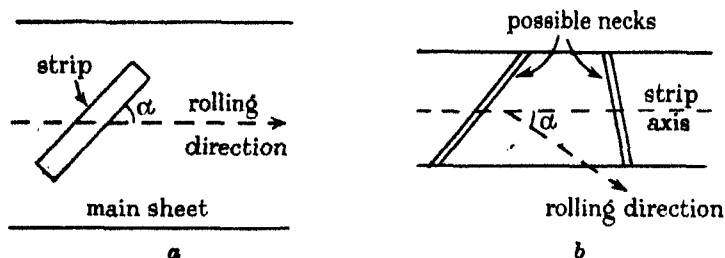


FIGURE 1. Positions of the two possible necks in a flat strip cut from rolled sheet and pulled in tension.

Körber & Hoff plotted graphs giving the two necking angles as functions of α . Figure 2 indicates qualitatively the general trend of their results; in detail the graphs depended on the material used and reduction in rolling.

The ordinate scale represents the acute angle between the line of the neck and the strip axis; the abscissa measures α , which of course ranges from 0 to $\frac{1}{2}\pi$. It is convenient to distinguish the two possible necking directions according as they tend to lie with the fibre (i.e. the rolling direction) or across it. The full curve in the figure corresponds to necking across the fibre; the dashed curve corresponds to necking with the fibre. It will be seen that there are three values of α for which the two possible necks make the same angle with the strip axis, thus giving the graph a figure of eight appearance. In the main sheet the principal axes of anisotropy are along and transverse to the rolling directions, and normal to the sheet. Hence the equality of the necking angles when α is either 0 or $\frac{1}{2}\pi$ is what would be expected from symmetry considerations since the axes of anisotropy are then parallel to the sides of the strip. The reason for the coincidence of the angles for a certain intermediate α will become clear when we analyze the experiments theoretically.

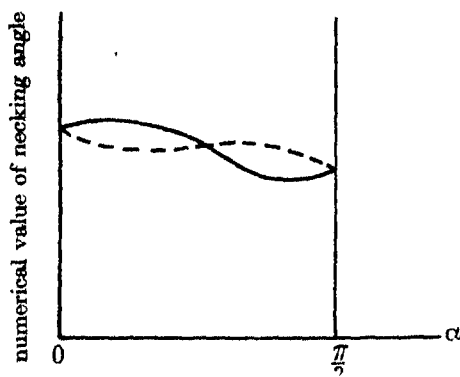


FIGURE 2. Qualitative representation of Körber & Hoff's measured values of the necking angle as a function of the angle α between strip axis and rolling direction. — across fibre; --- with fibre.

To begin with, consider a flat strip of isotropic metal strained in tension. Necking will begin after some preliminary extension at a point where there is a slight non-uniformity in the strip, either geometrical or structural. In view of the property of characteristics as directions along which small disturbances propagate, it is natural to suppose that the line of the neck will coincide with one or other of the two characteristics through the origin of the disturbance. If this origin lies not on the edge, but in the middle of the bar, a V-shaped neck is sometimes observed, with its branches coinciding with parts of both characteristics. We can immediately find the directions of the characteristics from equation (16) for a state of plane stress. Take the x axis in the direction of pulling and set $F = G = H = \frac{1}{3}N$ in view of the assumed isotropy. The directions of the characteristics are found to make an angle $\tan^{-1}\sqrt{2}$, or approximately 55° , with the strip axis. It has already been mentioned that the incremental extension in the characteristic directions is zero. The extension along the line of the neck is thus zero, and the neck forms by thinning in the thickness of the strip.

Orowan, in unpublished work on the pulling of isotropic strip, takes as a starting-point the assumption that necking will begin along a direction of zero extension; the final result for the necking angle is therefore the same. Körber & Siebel (1928) have also obtained this value by an entirely different argument which is, however, unconvincing.

When the strip is anisotropic and the anisotropy is uniformly distributed, let the x principal axis of anisotropy be taken along the fibre or rolling direction (figure 3). The x axis makes an acute angle α with the strip axis or pulling direction. The axis of z is as usual normal to the plane of the strip (i.e. to the plane of the paper in figure 3).

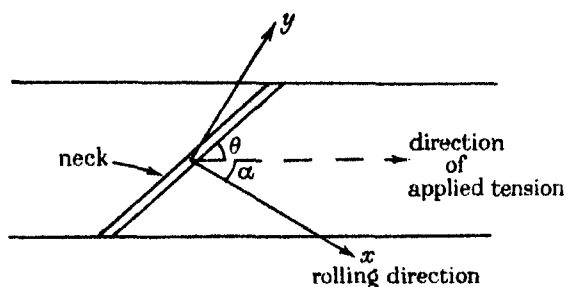


FIGURE 3. Co-ordinate system for analysis of the necking of flat strips in tension.

θ , measured from the axis in a sense away from the rolling direction denotes the inclination of a possible necking direction. It is the numerical value of θ that is plotted in figure 2. Except for material that has received very little cold work by rolling, the extension prior to necking is small compared with the rolling strains, and so the state of anisotropy in the strip at the beginning of necking will be effectively the same as in the rolled sheet. Let F , G , H , L , M , N , as in § 2, denote the anisotropic parameters specifying this state. If σ is the tensile stress in the strip when necking begins, the stress components referred to the x , y axes are

$$\sigma_{xx} = \sigma \cos^2 \alpha, \quad \sigma_{yy} = \sigma \sin^2 \alpha, \quad \sigma_{xy} = \sigma \sin \alpha \cos \alpha.$$

Inserting these in equation (16) with $dy/dx = \tan(\theta + \alpha)$ we obtain after some reduction:

$$a \tan^2 \theta + b \tan \theta - c = 0, \quad (17)$$

where

$$a = H + \sin^2 \alpha \cos^2 \alpha [(N - F - 2H) + (N - G - 2H)],$$

$$b = 2 \sin \alpha \cos \alpha [(N - F - 2H) \sin^2 \alpha - (N - G - 2H) \cos^2 \alpha],$$

$$c = F \sin^2 \alpha + G \cos^2 \alpha + H + \sin^2 \alpha \cos^2 \alpha [(N - F - 2H) + (N - G - 2H)].$$

By using (5) c can be shown to equal $1/\sigma^2$ and is therefore essentially positive for all values of α . a is positive except when $2N < F + G$. Since $N = 3F = 3G$ for an isotropic metal, the possibility of a being negative is most unlikely and can be

disregarded. There are therefore in general two distinct necks with different inclinations corresponding to the roots of this quadratic in $\tan \theta$. The roots are numerically equal, but opposite in sign when $b = 0$, which is true for $\alpha = 0$, $\frac{1}{2}\pi$, and for an intermediate value $\bar{\alpha}$ given by

$$\tan^2 \bar{\alpha} = \frac{N - G - 2H}{N - F - 2H}. \quad (18)$$

For these three values of α the two possible necks are symmetrically situated with respect to the strip axis. Since the neck is a direction of zero extension the principal axes of strain-increment are along and perpendicular to the axis for these three α -values, and so coincide with the principal stress axes. The theory thus predicts the figure of eight pattern of figure 2. For $\bar{\alpha}$ to be real, $(N - G - 2H)$ and $(N - F - 2H)$ must have the same sign and this condition must presumably have been satisfied for the materials used by Körber & Hoff. Further, if $(N - F - 2H)$ and $(N - G - 2H)$ are positive, the coefficient b is negative for $\alpha < \bar{\alpha}$ and positive for $\alpha > \bar{\alpha}$. Hence the sum $(-b/a)$ of the roots is positive for $\alpha < \bar{\alpha}$ and negative for $\alpha > \bar{\alpha}$. This means that the angle for necking across the fibre is numerically larger than that for necking with the fibre when $\alpha < \bar{\alpha}$, and vice-versa when $\alpha > \bar{\alpha}$. This agrees with the relative positions of the full and dashed curves in figure 2. If $(N - F - 2H)$ and $(N - G - 2H)$ are negative the curves are interchanged. We must therefore presume further that the anisotropy of the materials used by Körber & Hoff is such that

$$N > F + 2H, \quad N > G + 2H.$$

That there is nothing intrinsically impossible in these inequalities may be realized by remembering that $N = F + 2H = G + 2H$ when there is rotational symmetry of the anisotropy about the z axis.

The final feature of figure 2 which must be verified theoretically is that the general trend of Körber & Hoff's data was such that the figure of eight sloped downward from $\alpha = 0$ to $\alpha = \frac{1}{2}\pi$. Suppose θ_1 is the value of θ when $\alpha = 0$, and θ_2 the value when $\alpha = \frac{1}{2}\pi$. Then

$$\tan^2 \theta_1 = \frac{G}{H} + 1, \quad \tan^2 \theta_2 = \frac{F}{H} + 1.$$

By using the equations (6) it can be shown that the following possibilities arise, depending on the relative magnitude of the yield stresses X , Y , Z :

- (i) If $Z > X$, Y then $\theta_2 \leq \theta_1$, according as $X \leq Y$. Both θ_1 and θ_2 are less than 55° .
- (ii) If $Y > Z > X$ then $\theta_1 > 55^\circ > \theta_2$.
- (iii) If $X > Z > Y$ then $\theta_1 < 55^\circ < \theta_2$.

(iv) If X , $Y > Z$, then, if H is positive, $\theta_2 \leq \theta_1$ according as $X \leq Y$. Both θ_1 , θ_2 are greater than 55° . If H is negative the θ 's are imaginary and expansion occurs in the transverse direction; according to the theory necking should be inhibited.

It is found for many rolled metals that after severe reductions the yield stress in the rolling direction is less than that in the transverse direction. In particular this was observed by Körber & Hoff for the metals used by them. In the present

notation x is the rolling direction and so $Y > X$. The magnitude of Z was not measured. Now Körber & Hoff found $\theta_1 > \theta_2$, and this, according to the above analysis, is required by $Y > X$. Their values of θ_1, θ_2 were distributed haphazardly about 55° and so the relative magnitude of Z must have varied similarly.

The theory is thus in agreement with the experimental data at all points where a test is possible. Closer quantitative agreement could not be checked without a knowledge of the absolute magnitudes of the anisotropic parameters.

6. THE EFFECT OF ANISOTROPY DEVELOPED IN A TORSION TEST

Consider a torsion test performed on an initially isotropic, thin-walled, cylinder. Let us fix attention on a small element of the wall. In figure 4*a* the plane of the paper is to be regarded as tangential to the cylinder wall; AA' is the direction of shear and BB' is the axial direction.

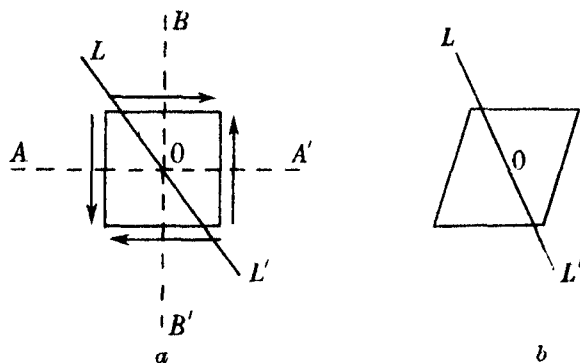


FIGURE 4. Deformation in pure torsion.

After twisting, the initially square element shears over into a parallelogram (figure 4*b*). An arbitrary direction LOL' fixed in the element rotates into a new position and simultaneously suffers a resultant extension or compression. For a given total shear it is clear that there will be some initial direction which undergoes most compression, and also one which undergoes most extension. A fibre structure will thus develop, and the principal axes of anisotropy in the plane of the wall at any moment can be expected to coincide approximately with the final positions of the directions of greatest extension and compression. These can be determined by a simple construction (figure 5). TT' is the direction of shear; ON , which can be taken of unit length, is the perpendicular on TT' from the centre O of an element. For a given total shear-strain γ there are two directions which undergo no resultant strain. One of these is clearly parallel to OT . If $DD' = \gamma$ and D, D' are reflexions in ON , then OD is the initial position of the other and OD' is its final position. This direction undergoes compression and then extension. Now let OC, OE be the internal and external bisectors of the angle between OT and OD . It is easy to prove

that OC is the initial position of the direction of greatest compression and OE is that of the direction of greatest extension. These directions are mutually orthogonal. The final position of OC is OC' where C' is the reflexion of E in ON : the final position of OE is OE' where E' is the reflexion of C in ON . OE' , OC' are of course the bisectors of the angle between OT' and OD' . Further, $OC' = DD' = EE' = \gamma$. We see therefore that, as the twist increases, the principal axes of anisotropy OE' , OC' rotate from positions making $\frac{1}{2}\pi$ with ON , TT' towards the limiting positions ON , OT' , and further that they vary relatively to the element itself. The degree of the anisotropy will also vary with progressive twisting, though not necessarily monotonically because of a possible complex Bauschinger effect due to alternate compression and extension.

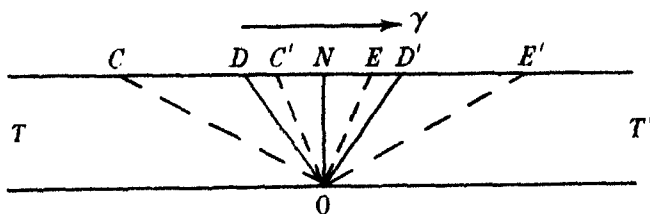


FIGURE 5. Construction for directions of greatest extension and compression in pure torsion.

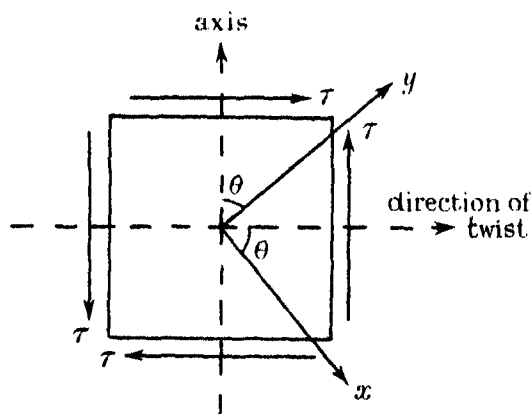


FIGURE 6. Co-ordinate system for analysis of the torsion of an anisotropic tube.

Suppose that at some stage during the torsion the x , y axes of anisotropy make an angle θ with the direction of twist and the cylinder axis (figure 6). As has been shown θ increases steadily from $\frac{1}{2}\pi$ towards $\frac{1}{4}\pi$. The x , y axes correspond respectively to $C'O$ and OE' in figure 5. Oy thus marks the fibre direction. If τ is the shear stress,

$$\sigma_{xx} = -\sigma_{yy} = -\tau \sin 2\theta, \quad \sigma_{xy} = \tau \cos 2\theta.$$

All other stress components are zero. The value of τ for which flow will continue is

$$\tau = [(F + G + 4H) \sin^2 2\theta + 2N \cos^2 2\theta]^{-\frac{1}{2}}. \quad (19)$$

The anisotropic parameters continually change in magnitude during the twisting because of work-hardening and varying anisotropy. The strain-increments are

$$\left. \begin{aligned} d\epsilon_{xx} &= -d\lambda(G + 2H)\tau \sin 2\theta, \\ d\epsilon_{yy} &= d\lambda(F + 2H)\tau \sin 2\theta, \\ d\epsilon_{zz} &= d\lambda(G - F)\tau \sin 2\theta, \\ d\epsilon_{xy} &= d\lambda N \cdot \tau \cos 2\theta. \end{aligned} \right\} \quad (20)$$

There is thus thinning or thickening of the cylinder wall. The strain-increment $d\epsilon_A$ in the axial direction is obtained by tensor transformation of the elements in (20):

$$d\epsilon_A = d\lambda \cdot \tau \sin 2\theta [(N - G - 2H) \sin^2 \theta - (N - F - 2H) \cos^2 \theta]. \quad (21)$$

With an ideally isotropic cylinder both the wall thinning and axial extension are of course zero.

Just after twisting is begun, when θ is a little larger than $\frac{1}{4}\pi$, the axial strain-increment has the sign of $(F - G)$ or of $(X - Y)$. In § 5 it was seen that in heavily rolled metals the yield stress along the fibre is usually less than that across the fibre. For small strains, when the anisotropy is still small, there seems to be no general rule. The cylinder may therefore shorten or lengthen initially according to the metal used. If for larger angles of twist we are entitled to assume as in § 5 that $N > G + 2H$, then $d\epsilon_A$ is finally positive. The most that can be said at present, then, is that shortening or lengthening of a torsion specimen, or even reversal of axial strain, are all *a priori* possible on the basis of the theory. Such changes in length have been observed by Swift (1947).

7. THE EARING OF DEEP-DRAWN CUPS

When a cup is deep drawn from a flat circular blank cut from rolled sheet, it is often found that the height of the rim above the base is not uniform, as would be expected in a symmetrical operation on an isotropic blank. Instead it is observed that 'ears' (to use the technical terminology) form in positions symmetrically situated with respect to the direction of rolling in the original sheet. Generally four ears occur, either at the ends of the two diameters making 45° with the rolling direction, or at the ends of the diameters making 0 and 90° with the rolling direction. The positions and height of the ears which are observed in any given instance depend among other things on the particular metal and on the prior mechanical and heat treatment (see, for example, Wilson & Brick 1945). Both types of earing can be produced in the same metal by suitably varying the treatment before drawing, e.g. in copper and steel (Barrett 1943). With brass, six ears have also been observed in the 0 and 60° positions (Cook 1937). In a few instances other earing positions have been reported (e.g. Cook & Richards 1943). It is recognized that the presence of earing is due to anisotropy in the rolled sheet, and several inconclusive attempts have been made to correlate the observed behaviour with the crystal texture and the mechanical properties of the material. The present approach is somewhat

different. The anisotropy is specified by the six parameters of the theory, whose values are related in some complicated way to the previous treatment of the material. The earing positions can, in principle, be calculated in terms of these parameters and the stresses and strains characterizing the deep-drawing process.

Earing begins while the blank is being drawn towards the shoulder of the die, and it is observed that the final positions of the ears coincide approximately with their initial positions (Wilson & Brick 1945). It is probably sufficient, therefore, to analyze the stress and strain distribution immediately after drawing begins, when the rim has just started to move towards the die aperture. A complete analysis of the whole process which allows adequately for the gradual formation of the ears is, in any event, hardly possible. In the initial stages of drawing, the action of the blank-holder must be considered in any calculation of the stresses. There are two main ways in which a blank-holder may be used: it may be held in a fixed position, or it may be pressed against the sheet by a constant load. Possibly a blank-holder may not even be used at all. It seems that the role of the blank-holder in connexion with earing has not been considered; the subsequent analysis indicates its importance. During the process the material eventually forming the wall of the cup is drawn towards the die aperture, undergoing circumferential compression and radial extension. A thickening of the sheet may also occur during this stage, depending on the constraint exerted by the blank-holder. Two extreme situations will be considered in the analysis. In the first the blank-holder is supposed fixed in a position such that the space between the holder and the die is equal to the original sheet thickness. In the second it is supposed either that no holder is used, or that the space between the holder and die is so much wider than the sheet thickness that negligible normal force is exerted in the early stages. If friction can be neglected, the first case corresponds to a state of plane strain, and the second to a state of plane stress. The case when a fixed load is applied to the blank-holder will lie somewhere between these extremes.

It is assumed that the ears begin to form at those points on the rim where the radial direction is one of the principal axes of the strain-increment. This seems reasonable in view of the approximate symmetry of the deformation about the tip of an ear. For consistency it must also be assumed that the hollows between the ears begin to form at points having the same property. On the rim the circumferential stress is the only non-zero stress component in the plane of the sheet. Hence the positions of the ears and hollows correspond to the points at which the principal axes of stress and strain-increment coincide.

Let axes of reference be chosen to coincide with the principal directions of anisotropy in the sheet. The z axis is taken normal to the blank, and the x axis along the direction of rolling. If the blank is drawn under conditions of plane strain, it follows from the discussion in § 4 that the ears and hollows can only form in the 0 , 45 and 90° positions. These are also the directions for which the uniaxial yield stress in plane strain has maximum and minimum values. From elementary considerations it is clear either that four ears form in the 0 and 90° positions with hollows in the 45°

positions, or that the reverse situation occurs. This will depend on the state of anisotropy. If the drawing occurs under conditions of plane stress then the discussion in § 4 shows that the ears and hollows can form only in the 0 and 90° positions and in positions making an angle ϕ with the rolling direction, where

$$\tan^2 \phi = \frac{N - F - 2H}{N - G - 2H}. \quad (22)$$

It must be remembered in deriving this equation that the state of stress on the rim is a tangential compression, so that $\phi = 90^\circ - \theta$, where θ is given by equation (14). According to § 4 the tangents at the points where the ears and hollows form are in the directions for which the yield stress in uniaxial tension has stationary values. Elementary considerations show, just as before, that there are four ears in the 0 and 90° positions, or in the ϕ positions. Notice that $\phi = 45^\circ$ when $F = G$ (i.e. $X = Y$), irrespective of the values of N and H . If, however, N is intermediate to $F + 2H$ and $G + 2H$, ϕ is not real and only two ears form either in the 0 or the 90° positions.

It does not seem possible to distinguish between the possible arrangements of the ears in terms of the relative magnitudes of the anisotropic parameters, without a solution for the displacements on the rim. Such a solution has not yet been found. Failing this it is tempting to surmise that the ears and hollows form respectively at points where the tangents to the rim are in the directions of the minimum and maximum values of the uniaxial yield stresses. This could be tested by experiment. It would be essential to perform plane strain or plane stress tensile tests, according to the conditions of drawing. Summing up the above analysis, the theory indicates that when the blank is drawn under conditions of plane strain, four ears will form in the 0 and 90° positions or in the 45° positions. When ears are found in other positions, this may be due either to friction or to the nature of the constraint applied by the blank-holder.

The author is indebted to Dr E. Orowan, F.R.S., for suggesting the undertaking of this research. The content of the paper owes much to many stimulating discussions with Dr Orowan during the course of the work.

The author is also indebted to the Chief Scientific Officer, Ministry of Supply, for permission to publish this paper.

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CORRIGENDUM

Proc. Roy. Soc. A, vol. 190, p. 370, equation (7)

For λ^3 read λ^2 .

Self-consistent field, with exchange, for nitrogen and sodium

BY D. R. HARTREE, F.R.S. AND THE LATE W. HARTREE

(Received 20 June 1947)

Wave functions for the normal configurations of neutral nitrogen and N^- have been calculated by the method of the self-consistent field with exchange (Fock's equations). To the accuracy of the approximation represented by these equations, the N^- ion would be unstable and liable to auto-ionization, but it is estimated that a better approximation of the treatment of a many-electron atom would give a small positive ionization potential for N^- .

Revised wave functions for Na^+ and the normal state of neutral Na have also been calculated.

Tables of results are given.

[*Note by D.R.H.* At the outbreak of war in September 1939, calculation of wave functions for a number of atoms, carried out by my father (W.H.), had been completed, but the results were still unpublished. Both he and I soon became occupied with other work, and the atomic structure calculations were laid aside. But to avoid the possibility of total loss of these results by enemy action, a copy was sent to Professor J. C. Slater at M.I.T., with a suggestion that he should, if possible, take steps to get them published in the U.S.A. so as to make them generally available. Professor Slater entrusted to Dr Millard F. Manning the preparation of these results for publication, and most of them were published, with some additional results by Manning, in the *Physical Review* (Hartree, Hartree & Manning 1941 *a, b, c*); I would like to take this opportunity of expressing my appreciation of the work of Dr Manning in this connexion. Dr Manning died in 1942, leaving a few of these results still unpublished, and so they remained, since the scientific personnel of the U.S.A., as of Britain, was by then mainly engaged on work more directly related to the allied war effort.

This paper presents the outstanding results for nitrogen (N^- and neutral) and sodium (Na^+). My father died in 1943 so that I have only his note-books to refer to in writing up the results. But the work seems straightforward, with no unusual features, and there is little to do but record the results.

Added in proof. Since writing this paper, I have found among my father's papers some calculations (without exchange) for Au; the results will be published separately.]

1. NITROGEN. WAVE FUNCTIONS

The normal electron configuration of neutral nitrogen (N^0) is $(1s)^2(2s)^2(2p)^3$, giving terms ^4S , ^2D , ^2P in that order (^4S deepest); that of N^- is $(1s)^2(2s)^2(2p)^4$ giving ^3P , ^1D , ^3S . Apart from the value of the atomic number, the equations are the same as for singly ionized oxygen and neutral oxygen respectively (Hartree, Hartree

& Swirles 1939, referred to as I). In the present work, superposition of configurations was neglected, so that these equations are obtained by putting $\mu = 0$ in equations (6) and (7) of I. Then, for each of the configurations mentioned, the different states are distinguished by the values of a single coefficient β , which has the following values (see I, table 1):

	N^0			N^-		
	^4S	^2D	^2P	^3P	^1D	^1S
β	$-\frac{2}{3}$	$-\frac{2}{3}$	0	$-\frac{2}{3}$	$-\frac{2}{3}$	0

Results for oxygen (I, § 5) show that the normalized radial wave functions P_N for the different terms arising from a single configuration are nearly linear in β , so for nitrogen the equations have only been solved for the extreme values of β for each configuration. The results are given in table 1. If values of P_N are required for intermediate values of β , they can be obtained by linear interpolation in β .

2. NITROGEN. ENERGY VALUES

The values of the various F and G integrals (see I, § 2) and ϵ -parameters occurring in the expression for the contribution to the energy from the $(2s)(2p)$ shell are given in table 2 (compare I, table 5); the coefficients with which these quantities occur in this expression are given in I, table 2 (column headed E_A ($\mu = 0$)). The values of the ϵ -parameters in table 2 were obtained in the course of the determination of the wave functions; the values of the F and G integrals were calculated from these wave functions. For the intermediate values of β ($-\frac{2}{3}$ for N^0 and $-\frac{2}{3}$ for N^-), values of the F and G integrals and ϵ -parameters were estimated by linear interpolation in β between the values in table 2.

From these quantities, the total energy of the $(2s)(2p)$ shell was calculated; the results are given in table 3. Since the values of some of the F integrals are multiplied by factors up to 8, the third decimal of the individual tabulated values is hardly significant, but it is retained since the calculated *ratio* of the inter-multiplet separations is probably reliable to an accuracy represented by 2 units in this place. Observed values of the ionization energy of the three states of neutral N are given in table 3. No calculated values are available for comparison, since no calculations were carried out for N^+ ; the purpose of including these observed values is to give a comparison between calculated and observed inter-multiplet separations.

The general character of the results for neutral N is very similar to that for O^+ (see I, table 7); the calculated ^2D - ^4S separation is slightly larger than that observed, whereas the calculated ^2P - ^2D separation is about 50 % larger than that observed, so that the calculated value of the ratio $(^2P-^2D)/(^2D-^4S)$ is 0.68, as compared with the observed value 0.50; to the accuracy of the calculated values, these figures are the same as for O^+ .

The results in table 3 show that, to the accuracy of the approximation on which these calculations are based, the N^- ion is unstable in the sense already defined else-

where (Hartree & Hartree 1938, § 1), namely that it is possible to find a solution to the equations, but the total energy of the configuration is greater than that for the neutral atom, so that the ion would be liable to auto-ionization. However, the calculated energy differences ($N^0, {}^4S$) - ($N^-, {}^3P$) is only -0.0641 atomic unit, and the results for oxygen suggest that this calculated value is likely to be too low by 0.08 atomic unit and probably more. Hence it seems probable that the lowest state, at least, of N^- is stable; whether the higher states arising from the normal configuration are stable or not is quite uncertain.

These results emphasize the importance of using as good an approximation to the general form of the wave function of a many-electron atom as is practicable, in calculations referring to negative ions. Fock's equations for the self-consistent field with exchange do not form a good enough approximation for the purpose; it is probably necessary explicitly to include in some way the dependence of the wave function on the mutual distances r_{ij} between the electrons, at least between those occupying the outer wave functions such as the $(2p)$ wave functions of O^- or N^- . The development of a means of doing this which leads to a practicable computing process is very much required in this context.

3. SODIUM (Na^+)

Sodium was the first atom for which solutions of Fock's equations were evaluated, this pioneer work being done by Fock & Petrashen (1934). Work on Na^- (Hartree & Hartree 1938) gave results for the core wave functions [$(1s)$, $(2s)$ and $(2p)$] which differed from Fock & Petrashen's wave functions for Na^+ by considerably more than was expected as a result of adding the $(3s)^2$ group to form Na^- , and considerably more, also, than the perturbation of the K^+ core on adding the $(4s)^2$ group to form K^- . Further, the differences between Fock & Petrashen's results for Na^+ and ours for Na^- were rather irregular, and separate examination of the two sets of results traced these irregularities to the Na^+ results.

Fock & Petrashen evaluated the solutions of the inhomogeneous differential equations for the radial wave functions with exchange by a method based on the use of the Green's function. This, while of course formally correct, does not seem the most suitable method for practical computation, and in view of the irregularities already mentioned, it seemed advisable to recalculate Na^+ by straightforward numerical integration. This, it must be emphasized, implies no criticism of Fock & Petrashen's work which, because of its pioneer character, was necessarily done without previous experience of handling these equations, and was a considerable achievement. Since then, however, much experience has been gained in the course of evaluating solutions of these equations for other atoms, and it seemed advisable to revise the results for Na^+ by calculations done in the light of all this experience.

The results are given in table 4, and show only small departures (0.002 at most in P_N) from those for Na^- , though the values of ϵ are considerably different on account of the contribution to the potential, in the region of the core of Na^- , from the $(3s)^2$

group. The differences from Fock & Petrashen's wave functions are, however, quite appreciable, up to 0.017 in $P(2s)$ and 0.014 in $P(2p)$. In view of the discrepancies from Fock & Petrashen's results, the work was done with particular care, and it is believed that the present results are correct to the accuracy of the calculations.

The $(3s)$ wave function for Na^0 was also calculated, taking the core wave functions tabulated in table 4; the result is included in table 4. It was found that to secure orthogonality of $P(3s)$ to $P(2s)$ a small but appreciable non-zero value of the non-diagonal parameter $\epsilon_{2s,3s}$ had to be taken ($\epsilon_{2s,3s} = 0.0045$).

Tables of results are given.

TABLE 1. NITROGEN. NORMALIZED WAVE FUNCTIONS

r	neutral N					N ⁻			
	P(1s)	$\beta = -\frac{3}{2}$ (⁴ S state)		$\beta = 0$ (² P state)		$\beta = -\frac{3}{2}$ (³ P state)		$\beta = 0$ (¹ S state)	
		P(2s)	P(2p)	P(2s)	P(2p)	P(2s)	P(2p)	P(2s)	P(2p)
0.00	0	0	0	0	0	0	0	0	0
0.01	0.327	0.072	0.0009	0.073	0.0009	0.070	0.0008	0.071	0.0008
0.02	0.611	0.134	0.0037	0.136	0.0036	0.130	0.0032	0.132	0.0031
0.03	0.855	0.187	0.0080	0.190	0.0079	0.182	0.0070	0.184	0.0068
0.04	1.064	0.232	0.0137	0.235	0.0135	0.225	0.0120	0.228	0.0117
0.06	1.389	0.300	0.029	0.304	0.0285	0.291	0.025	0.294	0.024 _s
0.08	1.615	0.343	0.048	0.347	0.047 _s	0.333	0.042	0.336	0.041
0.10	1.761	0.365	0.070 _s	0.370	0.069 _s	0.355	0.061 _s	0.359	0.060
0.12	1.845	0.371	0.095 _s	0.376	0.094	0.360	0.083	0.364	0.081 _s
0.14	1.880	0.363	0.122	0.368	0.120 _s	0.353	0.106	0.357	0.104
0.16	1.878	0.344	0.150	0.349	0.148	0.334	0.131	0.338	0.128
0.18	1.848	0.316	0.179	0.320	0.176 _s	0.307	0.156	0.310	0.153
0.20	1.797	0.281	0.209	0.285	0.206	0.273	0.182	0.276	0.178
0.25	1.613	0.172	0.283	0.174	0.279	0.168	0.247	0.169	0.242
0.30	1.393	0.047	0.356	0.047	0.350	0.046	0.310	0.046	0.304
0.35	1.173	-0.083	0.425	-0.084	0.417	-0.080	0.370	-0.081	0.363
0.40	0.969	-0.210	0.488	-0.212	0.479	-0.203	0.426	-0.205	0.417
0.45	0.789	-0.328	0.546	-0.332	0.535	-0.318	0.476	-0.321	0.467
0.50	0.636	-0.436	0.597	-0.441	0.585	-0.423	0.521	-0.427	0.511
0.6	0.404	-0.614	0.680	-0.621	0.665	-0.595	0.595	-0.602	0.582
0.7	0.250	-0.742	0.739	-0.750	0.722	-0.720	0.649	-0.728	0.634
0.8	0.153	-0.826	0.776	-0.833	0.758	-0.803	0.684	-0.811	0.668
0.9	0.092	-0.872	0.795	-0.878	0.776	-0.849	0.706	-0.856	0.689
1.0	0.055	-0.889	0.800	-0.894	0.781	-0.867	0.715	-0.874	0.698
1.1	0.033	-0.884	0.793	-0.888	0.775	-0.864	0.715	-0.870	0.698
1.2	0.019	-0.862	0.777	-0.865	0.761	-0.846	0.708	-0.850	0.690
1.4	0.007	-0.788	0.727	-0.788	0.717	-0.780	0.679	-0.782	0.663
1.6	0.003	-0.694	0.663	-0.692	0.659	-0.695	0.638	-0.693	0.624
1.8	0.001	-0.597	0.595	-0.593	0.596	-0.606	0.592	-0.602	0.582
2.0	—	-0.505	0.527	-0.499	0.534	-0.520	0.545	-0.515	0.538
2.2	—	-0.422	0.461	-0.415	0.473	-0.442	0.498	-0.436	0.496
2.4	—	-0.349	0.401	-0.342	0.417	-0.374	0.455	-0.366	0.456
2.6	—	-0.286	0.346	-0.280	0.366	-0.314	0.414	-0.306	0.418
2.8	—	-0.233	0.297	-0.228	0.320	-0.263	0.376	-0.255	0.383
3.0	—	-0.189	0.254	-0.184	0.278	-0.220	0.342	-0.211	0.352

TABLE 1 (cont.)

<i>r</i>	neutral N					N ⁻			
	<i>P</i> (1 <i>s</i>)	$\beta = -\frac{2}{3}$ (⁴ S state)		$\beta = 0$ (³ P state)		$\beta = -\frac{2}{3}$ (³ P state)		$\beta = 0$ (¹ S state)	
		<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)
3.2	—	-0.154	0.216	-0.149	0.241	-0.183	0.310	-0.175	0.323
3.4	—	-0.123	0.184	-0.119	0.208	-0.153	0.282	-0.145	0.296
3.6	—	-0.099	0.156	-0.095	0.180	-0.127	0.256	-0.120	0.272
3.8	—	-0.079	0.132	-0.076	0.155	-0.106	0.232	-0.100	0.250
4.0	—	-0.063	0.111	-0.060	0.133	-0.088	0.210	-0.083	0.230
4.5	—	-0.036	0.072	-0.034	0.090	-0.055	0.166	-0.052	0.189
5.0	—	-0.020	0.046	-0.019	0.060	-0.034	0.131	-0.032	0.155
5.5	—	-0.011	0.030	-0.011	0.040	-0.021	0.103	-0.020	0.127
6.0	—	-0.006	0.019	-0.006	0.026	-0.013	0.082	-0.013	0.105
6.5	—	-0.003	0.012	-0.003	0.017	-0.008	0.065	-0.008	0.087
7.0	—	-0.002	0.008	-0.002	0.011	-0.005	0.052	-0.005	0.072
8	—	—	0.003	—	0.005	-0.002	0.033	-0.002	0.049
9	—	—	0.001	—	0.002	-0.001	0.021	-0.001	0.034
10	—	—	—	—	0.001	—	0.013	—	0.024
11	—	—	—	—	—	—	0.008	—	0.016
12	—	—	—	—	—	—	0.005	—	0.011
14	—	—	—	—	—	—	0.002	—	0.005
16	—	—	—	—	—	—	0.001	—	0.002
18	—	—	—	—	—	—	—	—	0.001

TABLE 2. NITROGEN. *F* AND *G* INTEGRALS AND ϵ VALUES

β	N ^o		N ⁻	
	⁴ S	³ P	³ P	¹ S
	$-\frac{2}{3}$	0	$-\frac{2}{3}$	0
<i>F</i> ₀ (2 <i>s</i> , 2 <i>s</i>)	0.685	0.690	0.659	0.666
<i>F</i> ₀ (2 <i>s</i> , 2 <i>p</i>)	0.668	0.658	0.594	0.583
<i>F</i> ₀ (2 <i>p</i> , 2 <i>p</i>)	0.655	0.630	0.542	0.518
<i>F</i> ₂ (2 <i>p</i> , 2 <i>p</i>)	0.294	0.280	0.231	0.217
<i>G</i> ₁ (2 <i>s</i> , 2 <i>p</i>)	0.410	0.401	0.354	0.344
$\epsilon_{2s, 2s}$	1.890	1.958	1.161	1.250
$\epsilon_{2s, 2p}$	1.126	0.941	0.187	0.107

TABLE 3. NITROGEN. ENERGIES

N ^o		calculated total energy of (2 <i>s</i>) (2 <i>p</i>) shell		observed ionization energy	
N ^o	⁴ S	-9.651	92	0.535	88
	³ D	-9.559	63	0.447	44
	³ P	-9.496		0.403	
N ⁻	³ P	-9.587	54		
	¹ D	-9.533	89		
	¹ S	-9.444			

TABLE 4. SODIUM. NORMALIZED WAVE FUNCTIONS

Na ⁺				Na ⁰	Na ⁺				Na ⁰
<i>r</i>	<i>P</i> (1 <i>s</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (3 <i>s</i>)	<i>r</i>	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (3 <i>s</i>)	
0.00	0	0	0	0	3.2	-0.013	0.035	0.508	
0.01	0.629	0.154	0.004	0.023	3.4	-0.009	0.026	0.510	
0.02	1.128	0.274	0.014	0.041	3.6	-0.006	0.019	0.508	
0.03	1.517	0.366	0.030	0.055	3.8	-0.004	0.014	0.502	
0.04	1.814	0.433	0.050	0.065	4.0	-0.002 ₅	0.010	0.493	
0.06	2.192	0.507	0.102	0.076	4.5	-0.001	0.004 ₅	0.458	
0.08	2.356	0.517	0.163	0.077	5.0	—	0.002	0.414	
0.10	2.377	0.481	0.231	0.071	5.5	—	0.001	0.366	
0.12	2.305	0.412	0.302	0.060	6.0	—	0.000 ₅	0.318	
0.14	2.175	0.320	0.374	0.046	6.5	—	—	0.272	
0.16	2.012	0.215	0.444	0.030	7.0	—	—	0.230	
0.18	1.834	0.102	0.512	0.013	7.5	—	—	0.192	
0.20	1.652	-0.015	0.578	-0.005	8.0	—	—	0.160	
0.25	1.227	-0.301	0.724	-0.049	9	—	—	0.108	
0.30	0.878	-0.555	0.842	-0.087	10	—	—	0.072	
0.35	0.614	-0.763	0.933	-0.117	11	—	—	0.047	
0.40	0.422	-0.923	0.997	-0.138	12	—	—	0.030	
0.45	0.287	-1.037	1.039	-0.152	13	—	—	0.019	
0.50	0.194	-1.112	1.061	-0.158	14	—	—	0.012	
0.6	0.088	-1.169	1.061	-0.153	16	—	—	0.005	
0.7	0.040	-1.139	1.021	-0.131	18	—	—	0.002	
0.8	0.018	-1.061	0.956	-0.097	20	—	—	0.001	
0.9	0.008	-0.958	0.880	-0.058					
1.0	0.003	-0.846	0.799	-0.015					
1.1	0.001	-0.736	0.718	+0.028					
1.2	—	-0.632	0.640	0.072					
1.4	—	-0.455	0.501	0.156					
1.6	—	-0.319	0.385	0.232					
1.8	—	-0.220	0.292	0.297					
2.0	—	-0.149	0.219	0.354					
2.2	—	-0.101	0.163	0.400					
2.4	—	-0.068	0.121	0.437					
2.6	—	-0.045	0.089	0.466					
2.8	—	-0.030	0.065	0.487					
3.0	—	-0.020	0.048	0.501					
					Na ⁺				Na ⁰
					<i>P</i> (1 <i>s</i>)	<i>P</i> (2 <i>s</i>)	<i>P</i> (2 <i>p</i>)	<i>P</i> (3 <i>s</i>)	
					<i>r</i>	<i>r</i>	<i>r</i> ²	<i>r</i>	
					0.00	70.25	17.16	38.92	2.57 ₅
					0.01	62.94	15.36	36.85	2.30 ₅
					0.02	56.41	13.71	34.91	2.06
					0.03	50.57	12.21	33.09	1.83
					0.04	45.35	10.84	31.38	1.62
					<i>ε_{nl, nl}</i>	81.46	6.15 ₆	3.60 ₂	0.361

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The accuracy of atomic co-ordinates derived from Fourier series in X-ray crystallography. V

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In the first paper of this series, the effect of experimental errors in the Fourier coefficients, upon the derived atomic co-ordinates was investigated. The assumption was made that the probable errors were independent of the magnitudes of their parent Bragg reflexions.

It has been suggested that a more accurate assumption would be to take the probable error of any coefficient as being proportional to the magnitude of that coefficient. The present paper develops the theory on this basis, and a solution in closed form is obtained.

The question of how the experimental error in the co-ordinates varies with the position of the atom in relation to its neighbours is also investigated, and it is shown that the variation is much smaller than that previously derived for finite summation errors.

1. In the first paper of this series (Booth 1947*a*) it was shown that if, in the usual Fourier series

$$D(x, y, z) = \frac{1}{V} \sum_{-H}^{+H} \sum_{-K}^{+K} \sum_{-L}^{+L} |F(h, k, l)| \cos \left[2\pi \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) - \alpha(h, k, l) \right] \quad (1.1)$$

for the electron density $D(xyz)$ at any point (xyz) in a crystal lattice, the $|F|$ as determined by experiment are subject to a probable error Δe the probable error in the atomic co-ordinate is given by

$$\epsilon_x = \epsilon_y = \epsilon_z \leq \frac{0.66\Delta e}{N\sqrt{V}}, \quad (1.2)$$

where N is the atomic number of the particular atom.

The treatment which led to the above result was intended to give only an upper limit to the probable errors ϵ_x , etc., and whilst this is adequate in overall assessments of the excellence of a set of atomic co-ordinates it is often desirable to know which atoms, in any particular structure, are the most subject to experimental error. In addition the treatment has been criticized for assuming that the experimental error, Δe , is independent of the intensity of the parent plane.

It is the purpose of this paper to extend the treatment to the case in which errors are assumed to be proportional to the $|F|$ values of the parent reflexions, and also to investigate the manner in which the error varies with the position of an atom in the unit cell.

2. It was shown, in the treatment leading to (1.1), that an exact expression for ϵ_x is

$$\epsilon_x = -\frac{1}{NVa} \left(\frac{\pi}{p} \right)^{\frac{1}{2}} \left\{ \sum_H \sum_K \sum_L (\Delta F)^2 h^2 \sin^2(\theta - \alpha) \right\}^{\frac{1}{2}}, \quad (2.1)$$

where ΔF is the experimental error in the value of $F(hkl)$

$$\theta = 2\pi \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right),$$

$\alpha = \alpha(h, k, l)$ —the phase angle of the plane (hkl) —and the atomic density distributions near to atoms are assumed to be given by

$$d(x, y, z) = N \left[\frac{p}{\pi} \right]^{\frac{1}{2}} \exp \left(-p \{ (x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2 \} \right), \quad (2.2)$$

where N is the atomic number of the particular atom and p is approximately constant for light atoms.

Similar expressions hold for ϵ_y and ϵ_z .

If the proportionality of errors and Fourier coefficient envisaged in § 1 is made, so that

$$\Delta F = Pe, \quad (2.3)$$

where Pe is constant, (2.1) reduces to

$$\epsilon_x = -\frac{Pe}{NVa} \left(\frac{\pi}{p} \right)^{\frac{1}{2}} \left\{ \sum_{-H}^{+H} \sum_{-K}^K \sum_{-L}^L h^2 F^2 \sin^2(\theta - \alpha) \right\}^{\frac{1}{2}}. \quad (2.4)$$

Before evaluating the summation, further reduction has to be made to eliminate F and α . It was shown in part II that

$$\left. \begin{aligned} \tan \alpha &= \frac{\sum_{r=1}^N f_r \sin \theta_r}{\sum_{r=1}^N f_r \cos \theta_r}, \\ F^2(h, k, l) &= \left(\sum_{r=1}^N f_r \sin \theta_r \right)^2 + \left(\sum_{r=1}^N f_r \cos \theta_r \right)^2. \end{aligned} \right\} \quad (2.5)$$

$$\text{Whence} \quad F \sin \alpha = \sum_{r=1}^N f_r \sin \theta_r, \quad F \cos \alpha = \sum_{r=1}^N f_r \cos \theta_r. \quad (2.6)$$

Where, for the distribution (2.2),

$$f_r = N_r \exp \left(-\frac{\pi^2}{p} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] \right) \quad (2.7)$$

and the unit cell is assumed to contain N independent atoms.

Substitution from (2.6) in (2.4) yields

$$m\epsilon_x = -\frac{Pe}{N_m Va} \left(\frac{\pi}{p} \right)^{\frac{1}{2}} \left\{ \sum_{-H}^{+H} \sum_{-K}^K \sum_{-L}^L h^2 \left[\sum_{r=1}^N f_r \sin(\theta - \theta_r) \right]^2 \right\}^{\frac{1}{2}}, \quad (2.8)$$

the suffix m indicating that the error attached to the m th atom is being considered.

In view of the rapid convergence of the function f_r , defined by (2.7), the error involved in taking the limits (HKL) of (2.8) as infinite will be small, and the experimental errors will be nearly independent of the wave-length of the X-rays used to obtain the experimental data. Thus, using (2.7)

$$m\epsilon_x = -\frac{Pe}{N_m Va} \left(\frac{\pi}{p} \right)^{\frac{1}{2}} \left\{ \sum_{H=-\infty}^{+\infty} \sum_{K=-\infty}^{\infty} \sum_{L=-\infty}^{\infty} h^2 \exp \left(-\frac{2\pi^2}{p} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] \right) \left[\sum_{r=1}^N N_r \sin(\theta - \theta_r) \right]^2 \right\}^{\frac{1}{2}}. \quad (2.9)$$

An approximate value for the sum of the series can be found in the form of an integral, denoting the expression within the braces $\{\}$ by S ,

$$S \approx \iiint_{-\infty}^{+\infty} h^3 \left[\sum_{r=1}^N N_r \sin(\theta - \theta_r) \right]^2 \exp \left(-\frac{2\pi^2}{p} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] \right) dh dk dl. \quad (2.10)$$

Now

$$\begin{aligned} \left[\sum_{r=1}^N N_r \sin(\theta - \theta_r) \right]^2 &= \sum_{r=1}^N N_r^2 \sin^2(\theta - \theta_r) + 2 \sum_{\substack{r,s=1 \\ r>s}}^N N_r N_s \sin(\theta - \theta_r) \sin(\theta - \theta_s) \\ &= \sum_{r=1}^N \frac{1}{2} N_r^2 [1 - \cos 2(\theta - \theta_r)] + \sum_{\substack{r,s=1 \\ r>s}}^N N_r N_s [\cos(\theta_r - \theta_s) \\ &\quad - \cos(\theta - \theta_r + \theta - \theta_s)], \end{aligned} \quad (2.11)$$

from which it is seen that S (2.10) consists of four parts:

$$S = I_1 - I_2 + I_3 - I_4, \quad (2.12)$$

where

$$\begin{aligned} I_1 &= \sum_{r=1}^N \frac{N_r^2}{2} \iiint_{-\infty}^{+\infty} h^3 \exp \left(-\frac{2\pi^2}{p} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] \right) dh dk dl, \\ I_2 &= \sum_{r=1}^N \frac{N_r^2}{2} \iiint_{-\infty}^{+\infty} h^3 \cos 4\pi \left[\frac{h}{a} (x - x_r) + \frac{k}{b} (y - y_r) + \frac{l}{c} (z - z_r) \right] \\ &\quad \times \exp \left(-\frac{2\pi^2}{p} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] \right) dh dk dl, \\ I_3 &= \sum_{\substack{r,s=1 \\ r>s}}^N N_r N_s \iiint_{-\infty}^{+\infty} h^3 \cos 2\pi \left[\frac{h}{a} (x_r - x_s) + \frac{k}{b} (y_r - y_s) + \frac{l}{c} (z_r - z_s) \right] \\ &\quad \times \exp \left(-\frac{2\pi^2}{p} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] \right) dh dk dl, \\ I_4 &= \sum_{\substack{r,s=1 \\ r>s}}^N N_r N_s \iiint_{-\infty}^{+\infty} h^3 \cos 2\pi \left[\frac{h}{a} (x - x_r + x - x_s) + \frac{k}{b} (y - y_r + y - y_s) + \frac{l}{c} (z - z_r + z - z_s) \right] \\ &\quad \times \exp \left(-\frac{2\pi^2}{p} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] \right) dh dk dl. \end{aligned} \quad (2.13)$$

3. It is seen that all the integrals (2.13) can be derived from

$$I = \iiint_{-\infty}^{+\infty} h^3 \cos(Xh + Yk + Zl) \exp(-eh^2 - fk^2 - gl^2) dh dk dl. \quad (3.1)$$

Now

$$I = \int_{-\infty}^{+\infty} \exp(-gl^2) \int_{-\infty}^{+\infty} \exp(-fk^2) \int_{-\infty}^{+\infty} h^3 \cos(Xh + \mu) \exp(-eh^2) dh dk dl, \quad (3.2)$$

where

$$\mu = Yk + Zl. \quad (3.3)$$

Considering the first integration

$$\int_{-\infty}^{+\infty} h^2 \cos(Xh + \mu) \exp(-eh^2) dh = \int_{-\infty}^{+\infty} h^2 \cos Xh \cos \mu \exp(-eh^2) dh$$

since the integral involving $\sin(xh)$ is zero on account of the asymmetry of the integrand. Now

$$\int_{-\infty}^{+\infty} \cos(Xh) \exp(-eh^2) dh = \sqrt{\frac{\pi}{e}} \exp\left(-\frac{X^2}{4e}\right), \quad (3.4)$$

whence, differentiating both sides with respect to e ,

$$\int_{-\infty}^{+\infty} h^2 \cos(Xh) \exp(-eh^2) dh = \frac{1}{2e} \sqrt{\frac{\pi}{e}} \left[1 - \frac{X^2}{2e}\right] \exp\left(-\frac{X^2}{4e}\right). \quad (3.5)$$

Thus

$$I = \frac{1}{2e} \sqrt{\frac{\pi}{e}} \left[1 - \frac{X^2}{2e}\right] \exp\left(-\frac{X^2}{4e}\right) \int_{-\infty}^{+\infty} \exp(-gl^2) \int_{-\infty}^{+\infty} \cos(Yk + Zl) \exp(-fk^2) dk dl, \quad (3.6)$$

and, using (3.4) with suitable changes of symbols,

$$I = \frac{1}{2e} \sqrt{\frac{\pi}{e}} \sqrt{\frac{\pi}{f}} \sqrt{\frac{\pi}{g}} \left[1 - \frac{X^2}{2e}\right] \exp\left(-\frac{1}{4} \left[\frac{X^2}{e} + \frac{Y^2}{f} + \frac{Z^2}{g}\right]\right). \quad (3.7)$$

4. Using the integral (3.7) the values of (2.13) can be written down.

$$\left. \begin{aligned} I_1 &= \sum_{r=1}^N \frac{a^2 V}{4\pi} N_r^2 \left(\frac{p}{2\pi}\right)^{\frac{1}{2}}, \\ I_2 &= \sum_{r=1}^N \frac{a^2 V}{4\pi} N_r^2 \left(\frac{p}{2\pi}\right)^{\frac{1}{2}} [1 - 4p(x - x_r)^2] \exp(-2p[(x - x_r)^2 + (y - y_r)^2 + (z - z_r)^2]), \\ I_3 &= \sum_{\substack{r,s=1 \\ r>s}}^N \frac{a^2 V}{2\pi} N_r N_s \left(\frac{p}{2\pi}\right)^{\frac{1}{2}} [1 - p(x_r - x_s)^2] \exp\left(-\frac{p}{2}[(x_r - x_s)^2 + (y_r - y_s)^2 + (z_r - z_s)^2]\right), \\ I_4 &= \sum_{\substack{r,s=1 \\ r>s}}^N \frac{a^2 V}{2\pi} N_r N_s \left(\frac{p}{2\pi}\right)^{\frac{1}{2}} [1 - p(x - x_r + x - x_s)^2] \\ &\quad \times \exp\left(-\frac{p}{2}[(x - x_r + x - x_s)^2 + (y - y_r + y - y_s)^2 + (z - z_r + z - z_s)^2]\right). \end{aligned} \right\} \quad (4.1)$$

Whence, from (4.1), (2.12), (2.10) and (2.9),

$$\begin{aligned} m\epsilon_x &= -\frac{Pe}{2N_m \sqrt{V}} \left(\frac{\pi}{2p}\right)^{\frac{1}{2}} \left\{ \sum_{r=1}^N N_r^2 - N_r^2 [1 - 4p(x_m - x_r)^2] \right. \\ &\quad \times \exp(-2p[(x_m - x_r)^2 + (y_m - y_r)^2 + (z_m - z_r)^2]) + 2 \sum_{\substack{r,s=1 \\ r>s}}^N N_r N_s [1 - p(x_r - x_s)^2] \\ &\quad \times \exp\left(-\frac{p}{2}[(x_r - x_s)^2 + (y_r - y_s)^2 + (z_r - z_s)^2]\right) - N_r N_s [1 - p(x_m - x_r + x_m - x_s)^2] \\ &\quad \times \exp\left[-\frac{p}{2}[(x_m - x_r + x_m - x_s)^2 + (y_m - y_r + y_m - y_s)^2 + (z_m - z_r + z_m - z_s)^2]\right] \Big\}^{\frac{1}{2}}, \end{aligned} \quad (4.2)$$

with exactly similar expressions for $m\epsilon_y$ and $m\epsilon_z$.

For the purpose of calculation it is more convenient to consider, not the components of error, ϵ_x , ϵ_y and ϵ_z , but the total error ϵ_m , defined by:

$$\epsilon_m^2 = {}_m\epsilon_x^2 + {}_m\epsilon_y^2 + {}_m\epsilon_z^2. \quad (4.3)$$

Equations (4.2) show that

$$\begin{aligned} \epsilon_m = \pm \frac{Pe}{2N_m\sqrt{V}} \left(\frac{\pi}{2p} \right)^{\frac{1}{2}} & \left\{ \sum_{r=1}^N 3N_r^2 - N_r^2[3 - 4pR_{mr}^2] \exp(-2pR_{mr}^2) \right. \\ & + 2 \sum_{\substack{r,s=1 \\ r>s}}^N N_r N_s [3 - 4p(\frac{1}{2}R_{rs})^2] \exp(-2p(\frac{1}{2}R_{rs})^2) \\ & \left. - N_r N_s [3 - 4pR_{mrs}^2] \exp(-2pR_{mrs}^2) \right\}^{\frac{1}{2}}, \end{aligned} \quad (4.4)$$

$$\begin{aligned} \text{where } R_{pq}^2 &= (x_p - x_q)^2 + (y_p - y_q)^2 + (z_p - z_q)^2, \\ R_{mrs}^2 &= [x_m - \frac{1}{2}(x_r + x_s)]^2 + [y_m - \frac{1}{2}(y_r + y_s)]^2 + [z_m - \frac{1}{2}(z_r + z_s)]^2. \end{aligned} \quad (4.5)$$

This suggestive notation shows that, on account of the rapid evanescence of the exponentials with increasing values of R , only nearest neighbour atoms need be considered in summations involving m .

5. An evaluation of the errors predicted by (4.4) for some actual molecular configurations shows that, in three-dimensional synthesis where very close approach of atomic maxima is prohibited, all terms in the summations, except R_{mm} , are negligible. The simplified formula

$$\epsilon_m = \pm \frac{Pe}{2\sqrt{V}} \left(\frac{\pi}{2p} \right)^{\frac{1}{2}} \left\{ \sum_{r=1}^N 3\omega_r^2 \right\}^{\frac{1}{2}} \quad (5.1)$$

proves to be adequate. Here ω_r is the 'weight' (N_r/N_m) of the r th atom with respect to the atom m under consideration, and the prime indicates that the term $r = m$ is to be omitted from the summation.

For structures containing only atoms of approximately equal atomic numbers the formula

$$\epsilon_m = \pm \frac{Pe}{2} \left(\frac{\pi}{2p} \right)^{\frac{1}{2}} \left\{ \frac{3(N-1)}{V} \right\}^{\frac{1}{2}} \quad (5.2)$$

is adequate. Thus, for a benzene ring configuration, the expression in braces $\{\}$ of (5.2) has the value $(15/V)$ against the exact value, given by (4.5), $(14.65/V)$.

6. For completeness, the modifications of (4.4) for two- and one-dimensional summations have been derived, and it is found that all the results can be summarized in the formula

$$\begin{aligned} \epsilon_m = \pm \frac{Pe}{2N_m\sqrt{v}} \left(\frac{\pi}{2p} \right)^{\frac{1}{2}(2+n)} & \left\{ \sum_{r=1}^N nN_r^2 - N_r^2(n - 4pR_{mr}^2) \exp(-2pR_{mr}^2) \right. \\ & + 2 \sum_{\substack{r,s=1 \\ r>s}}^N N_r N_s [n - 4p(\frac{1}{2}R_{rs})^2] \exp(-2p(\frac{1}{2}R_{rs})^2) \\ & \left. - N_r N_s [n - 4pR_{mrs}^2] \exp(-2pR_{mrs}^2) \right\}^{\frac{1}{2}}, \end{aligned} \quad (6.1)$$

where n = number of dimensions in summation,

v = generalized 'volume' of repeat unit,

= volume for 3-dimensional summations,

= area for 2-dimensional summations,

= length for 1-dimensional summation.

In a like manner (5.1) and (5.2) can be extended, but, since in projection approach to coincidence is possible, their use is limited and care must be exercised to ensure their validity.

$$(5.1) \text{ becomes } \epsilon_m = \pm \frac{Pe}{2\sqrt{v}} \left(\frac{\pi}{2p} \right)^{\frac{1}{2}(2+n)} \left\{ \sum_{r=1}^N n\omega_r^2 \right\}^{\frac{1}{2}}, \quad (6.2)$$

$$\text{and (5.2) } \epsilon_m = \pm \frac{Pe}{2} \left(\frac{\pi}{2p} \right)^{\frac{1}{2}(2+n)} \left\{ \frac{n(N-1)}{V} \right\}^{\frac{1}{2}}. \quad (6.3)$$

7. An attempt has been made to obtain a value for the most probable proportional error, Pe in the case of oxalic acid. A comparison of the experimental $F(hkl)$ values for this substance, obtained independently by Robertson & Woodward (1936) and by Brill, Hermann & Peters (1942), gave a value:

$$Pe = 0.36,$$

but the fit of the data to a normal error curve was much less satisfactory than that obtained for the *absolute* error which gave (Booth 1947b)

$$\Delta e = 0.82.$$

The errors in co-ordinates, predicted by the absolute and proportional error formulae respectively are, for oxalic acid

$$\epsilon = 0.01_0 A, \quad \epsilon = 0.01_7 A.$$

So that it is seen that the present treatment suggests errors approximately twice as large as the more naïve methods of part I. At the same time it must be remembered that the method of summation, via an infinite integral, includes all terms possibly included in the Fourier summation for electron density, i.e. makes the limits H, K, L , in (1.1) infinite. The same assumption in the simple treatment with absolute errors would result in an infinite error in the atomic co-ordinate. The correct solution undoubtedly lies somewhere between the two alternatives.

The method of the present paper is easily extended to any law of variation of error with Bragg angle of reflexion and should such a law be found, which was in good accord with observation, it might prove worthwhile to attempt the integrations—although the probability of a result in closed form is small and approximate methods would have to be used.

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A study of the interaction of radio waves

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Experiments are described in which the phenomenon of wave-interaction ('Luxembourg effect') is used to provide information about the height at which radio waves of different frequencies are absorbed in the ionosphere. It is first demonstrated by two crucial experiments that the absorption mechanism suggested by Bailey & Martyn (1934 *a* and *b*) is the true one.

Measurements of the phase of the modulation transferred from one wave to the other by the non-linear absorption process in the ionosphere are described; and it is shown how, by measuring this phase at different modulation frequencies, it is possible to locate the region where the interaction occurs. The results of a series of experiments summarized in tables 2, 3*a* and 3*b* and figures 8 and 9 are discussed.

The conclusion is reached that the frequency with which electrons collide with neutral molecules at a height of about 85 km. is of the order $5 \times 10^8 \text{ sec.}^{-1}$, and that this is the height near which the main absorption of waves of frequency 1 Mcyc./sec. and 200 keyc./sec. are absorbed at night. Waves of frequency 90 and 68 keyc./sec. are absorbed, and possibly also reflected, below this level. With the approach of dawn the regions responsible for absorbing 1 Mcyc./sec. and 200 keyc./sec. waves drift apart.

The theory of Bailey & Martyn (1934*b*) and Bailey (1937*a*) is related to modern theories of ionospheric absorption and is restated with the standard nomenclature of Appleton's magneto-ionic theory.

1. INTRODUCTION

It is well known that a radio wave travelling through the ionosphere may, under certain circumstances, interact with a second wave in such a way that a modulation imposed on one of them becomes transferred to the other. This effect has been called 'wave-interaction' or, sometimes, the 'Luxembourg effect' because the first observations of the effect were made with one set of waves sent out from the broadcasting station at Luxembourg. In those examples of this phenomenon which were first observed the interaction produced unwanted modulation superimposed on the modulation of the radio station which it was desired to receive. It was therefore natural to call the wave whose reception was desired the *wanted wave* and that from which the undesired modulation was transferred was called the *interacting wave*. We shall preserve this nomenclature throughout this paper: it is illustrated schematically in figure 1.

Many experiments have been made to investigate wave-interaction, and especially to discover the factors which determine its magnitude (van der Pol & van der Mark (1935); van der Pol (1935); Batimier & Pfitzer (1935); Grosskopf (1938); and Huxley, Foster & Newton (1947)). Interaction has so far been observed only with wavelengths in the broadcast band (200 to 1500 m.) where it has been found with wanted and interacting stations both in the medium-wave band, both in the long-wave

band, or with one in each band. In the latter case the wanted wave may be either in the medium-wave or the long-wave band.

To produce interaction, the ionosphere must behave as a 'non-linear' transmission medium, and Bailey & Martyn (1934*a*) have suggested that the absorption of the waves provides the necessary non-linearity. They first put forward their suggestion before ideas about the ionospheric absorption of waves were very clear; their theory may now be restated as follows. The main absorption of the wanted wave occurs over fairly well-defined portions of the trajectory which are at a level different from that where the main bending takes place. This absorption depends on the frequency with which electrons collide with neutral molecules, and anything which increases the velocity of the electrons, and therefore the frequency of these collisions, will increase the absorption. If now another wave (the interacting wave) is absorbed in the same place the energy removed from it will increase the velocity

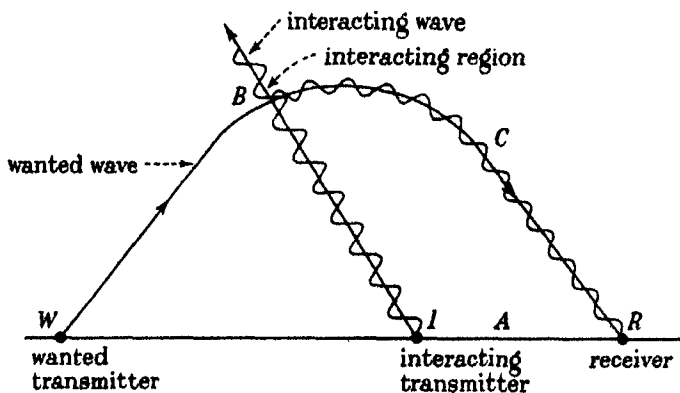


FIGURE 1. Schematic diagram to illustrate nomenclature.

of the electrons,* and therefore the frequency of their collisions, with the result that the wanted wave will be more strongly absorbed. In the presence of the interacting wave the wanted wave will therefore be weaker. If the amplitude of the interacting wave is now slowly varied periodically the velocity of the electrons will follow in step, and the absorption of the wanted wave will also vary periodically: in this way the modulation of the interacting wave will become superimposed on the wanted wave. According to the theory of Bailey & Martyn this is the mechanism of wave interaction.

If the interacting wave were suddenly removed the velocities of the electrons would fall exponentially to their normal values with a time-constant which would depend on the energy lost by an electron at each collision. We shall call this time-constant the 'relaxation time' of the electrons and shall denote it by τ ; we shall

* It is interesting to note that a 100 kW transmitter working on a frequency of 200 kcyc./sec. is capable of increasing the temperature of the electrons in the appropriate part of the ionosphere by about 2% (see §6(*a*)).

see later that its magnitude is of the order of 10^{-3} sec. If the modulation frequency is increased so that it becomes comparable with $(2\pi\tau)^{-1}$ then the electrons will begin to be incapable of following the modulation and the interaction will become smaller. For slow variations the electrons' velocity will vary in phase with the modulation of the interacting wave; as the frequency is increased, however, the electrons' velocity will tend to lag in phase behind the modulation of the wave, and when the frequency is great the phase-lag will be $\frac{1}{2}\pi$.*

The original papers of Bailey & Martyn contained the deductions mentioned above, but the theory is here restated in detail in § 6 and appendix A in a form which relates it more closely to modern theories of the ionosphere. If the theory is correct it might be expected that an experimental study of wave interaction would yield valuable information about the absorbing portions of the ionosphere, and in particular about those parts of the ionosphere which absorb both waves strongly. It is the purpose of this paper to describe experiments made with this object, and to discuss the results obtained.

Before the present work was started the only experimental test of the theory of Bailey & Martyn was one in which the amplitude of the transferred modulation was measured at different frequencies (van der Pol & van der Mark 1935). It was found that the shape of the curve relating amplitude and frequency agreed with the theory but the test was admittedly somewhat indirect, and van der Pol stated (van der Pol 1934):

'Finally in our opinion it cannot be considered to have been proved definitely that the effect is of a typical non-linear nature. The possibility is still open for an explanation on the basis of a Doppler effect, viz. the periodic raising of the conducting layers of the ionosphere in the rhythm of the modulation of the unwanted station and restored by the molecular agitation, thus causing a frequency or phase modulation of the wanted wave, which may in turn cause an amplitude modulation at the receiver due to the superposition of this frequency modulated wave with other rays which have not been affected on their course.'

It therefore seemed desirable to make a more direct test of the absorption hypothesis, and two such tests are described in § 3. The first of these consisted in switching the interacting wave on and off and observing that the wanted wave was weaker in the presence of the interacting wave. The second was suggested by Appleton (1938) and involved a comparison, at low modulation-frequencies, of the phases of the modulation received direct on the interacting wave and received after being transferred to the wanted wave by the process of wave-interaction. Both these tests supported the hypothesis of the absorption mechanism.

Once interaction had been demonstrated by switching the interacting wave on and off it was no longer necessary to modulate that wave to make observations, and it was therefore possible to use wave-lengths outside the broadcast band, where the transmitting stations available are not usually capable of being modulated. Experiments on these wave-lengths are described in § 5.

* For a proof of these statements see appendix A.

When a modulated interacting wave was used interesting information was obtained by varying the modulation frequency and comparing the phase of the modulation received direct from the interacting station with that of the modulation transferred to the wanted wave. As the frequency is changed the phase difference changes for two different reasons: (a) the phase change associated with the relaxation time occurs as previously described, and as analyzed in detail in appendix A; and (b) a progressive phase change occurs associated with the different lengths of the two paths labelled *IAR* and *IBCR* in figure 1. It has proved possible to separate the two different effects and to deduce separately the relaxation time of the electrons and the difference between the paths *IBCR* and *IAR*. The path *WBCR*, of the wanted wave, was determined, in a separate experiment, by causing the transmitter of the wanted wave to emit pulses of the type usual in ionospheric research and it was then possible to locate the region (*B*) of interaction. Experiments based on the principles here outlined are described in § 4.

In the estimation of the relaxation time of the electrons it is also of value to observe the way in which the amplitude of the imposed modulation varies with frequency. A special method developed for measuring this amplitude is described in § 5.

The evidence from the different types of experiment is collected and discussed in § 7. In this discussion we shall make use of a quantity which we have called the 'coefficient of transferred absorption' which is a measure of the fractional decrease which occurs in the field strength of the wanted wave when a steady interacting wave is suddenly switched on.

2. ARRANGEMENT OF TRANSMITTERS AND RECEIVERS

For experiments of this kind it is necessary to use transmitters of suitable wave-length and considerable power situated in suitable places, and we were most fortunate in obtaining the enthusiastic co-operation of the B.B.C., who provided the necessary transmissions. We wish to record our thanks to the Chief Engineer and all those on his staff who helped in the organization and carrying out of the complicated series of experimental transmissions for which we asked and, in particular, we should like to thank Mr H. L. Kirke, head of the B.B.C. Research Department, for his willingness to help on all occasions. We also wish to thank the Chief Engineer of the Post Office and his staff, and the Director of Scientific Research at the Admiralty, for putting their most valuable facilities at our disposal. Without the help of these organizations the series of experiments here described would have been impossible.

The main series of observations was made at Cambridge (lat. $00^{\circ}05'W.$, long. $52^{\circ}10'N.$). Dr L. G. H. Huxley made some additional observations on the same transmissions at Birmingham and we have had the benefit of comparing his results with ours. The transmitters which were used at different times are listed in table 1 and their positions indicated in the map of figure 2.

TABLE 1. DETAILS OF TRANSMITTERS USED

name or call sign	place	lat. and long.	designation on map of figure 2	controlling authority	power in kW	frequency in kcy./sec.	nature of trans- mission
Ottringham	Ottringham	00° 04' W. 53° 42' N.	O	B.B.C.	167	167	modulated
Droitwich	Droitwich	02° 06' W. 52° 18' N.	D(200)	B.B.C.	150	200	modulated
Westerglen	Westerglen	03° 49' W. 55° 59' N.	W	B.B.C.	60	767	modulated
Lisnagarvey	Lisburn	06° 03' W. 54° 29' N.	L	B.B.C.	100	1050	modulated
Droitwich	Droitwich	02° 06' W. 52° 18' N.	D(1013)	B.B.C.	68	1013	modulated
GBY	Rugby	01° 20' W. 52° 15' N.	GBY	Post Office	80	60	single sideband telephony
GYA 2	Cleethorpes	00° 10' W. 53° 30' N.	GYA 2	Admiralty	20	90.2	keyed

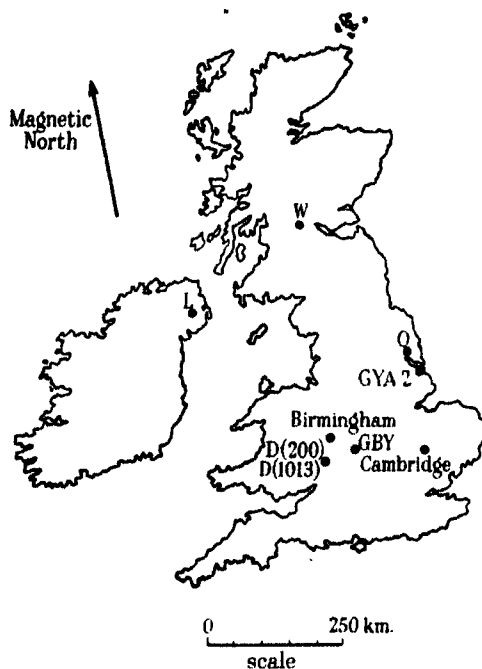


FIGURE 2. Locations of transmitters and receivers

3. TESTS OF THE ABSORBING MECHANISM

If wave interaction is explained by the absorption theory of Bailey & Martyn, then when the interacting wave is strong we should expect the wanted wave to be weak, and Appleton (1938) has pointed out that the modulation of the interacting wave and the modulation imposed on the wanted wave should therefore be in antiphase. It is shown in the next section that this antiphase relationship would only be expected if the modulation frequency were low enough, and it is demonstrated that a frequency of 50 cyc./sec. satisfies the necessary conditions. Special attention has therefore been paid to the observation of the phases at this frequency. On all occasions, and with all the combinations of wanted and interacting transmitters which are described later, it has been found that the modulation received direct from the interacting station is in opposite phase to that transferred to the downcoming wave from the wanted station.* This observation provides one fundamental check of the absorption theory of wave-interaction.

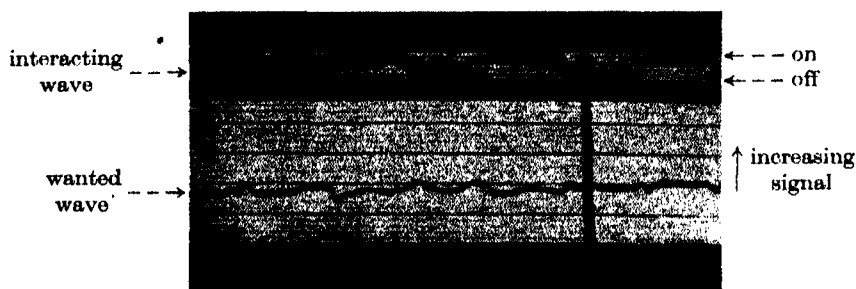


FIGURE 3. Effect of switching the interacting station on and off. In this record the wanted signal is fed to the recording galvanometer through a condenser so that only the sudden changes of amplitude, at the instants of switching the interacting wave on or off, are recorded.

A further very direct test of the absorption theory is provided by arranging that the sender of the interacting wave is not modulated, but is simply switched on and off. When it is on the wanted wave should be weaker and when it is off it should be stronger. This test has been made with the two combinations of (a) Westerglen (wanted) and Ottringham (interacting); and (b) Lisnagarvey (wanted) and Droitwich 200 kyc./sec. (interacting). The change of amplitude was measured by observing the rectified current on a galvanometer arranged so that the greater part of the standing current was 'backed off'. The wanted wave was always fading and it was necessary to keep the 'backing off' arrangement adjusted by hand so that the reading was always on the scale of the galvanometer. There was a clearly marked decrease of amplitude when the interacting station was switched on and an increase when it was switched off, as required by the theory.

* In appendix B we discuss some complications which may arise if a ground wave is received in strength comparable with the downcoming wave.

The change in amplitude ΔF of the radio-frequency e.m.f. was determined as a fraction of the total e.m.f. F . We shall call the fraction $\Delta F/F$ the 'coefficient of transferred absorption', and its magnitude will be further discussed in § 5.

Although the method of the 'backed-off' galvanometer proved most satisfactory for measurement of the change of amplitude, the occurrence of fading rendered it less useful for providing a permanent record of the effect. A photographic record was therefore obtained by the use of a rapidly moving galvanometer which was fed from the receiver through a condenser of such a value that the slower changes representing fading were less evident in comparison with the rapid changes produced by keying the interacting transmitter. A record obtained in this way is reproduced in figure 3.

The success of these two very direct tests of the absorption theory of interaction has satisfied us that the theory is correct, and has encouraged us to use it in making the detailed deductions explained in the rest of this paper.

4. OBSERVATIONS OF PHASE

Since it was desired to compare the phase of the transferred modulation with that of the wave received over a known direct path from the interacting station, it was essential to ensure that the downcoming wave alone was received from the wanted station and the ground wave alone from the interacting station. In the two main series of experiments to be described in this section the transmitter of the wanted wave was either Westerglen (frequency 767 kyc./sec., distance 480 km.) or Lisnagarvey (frequency 1050 kyc./sec., distance 495 km.) and, since the experiments were all done during the night or at dawn, the downcoming wave was considerably stronger than the ground wave. It was therefore sufficient to receive it on a simple aerial; a loop was often used so that its directional properties could be used to reduce interference from other transmissions. In some subsidiary experiments the wanted station was nearer (e.g. Droitwich distant 180 km., transmitting either on 1013 kyc./sec. or on 200 kyc./sec.) and in order to receive only the downcoming wave it was necessary to use a loop aerial adjusted, by day, to suppress the ground-wave.

In the main series of experiments the interacting transmitter was in the long-wave band and was distant 100 or 200 km. so that its ground wave was considerably stronger than the downcoming wave. A vertical aerial, which discriminates to some extent against the downcoming wave, was always used. No deductions about phase were made from any subsidiary experiments in which the interacting station produced a strong downcoming wave at the receiver.

The two waves were received on two separate radio-frequency amplifiers (three stages of straight amplification) each followed by a diode detector and one stage of audio-frequency amplification. The audio-frequency amplifiers were designed so that their response was constant over the range 50 to 2000 cyc./sec. and so that the phase-shift introduced by them was small. Moreover, both amplifiers were similar

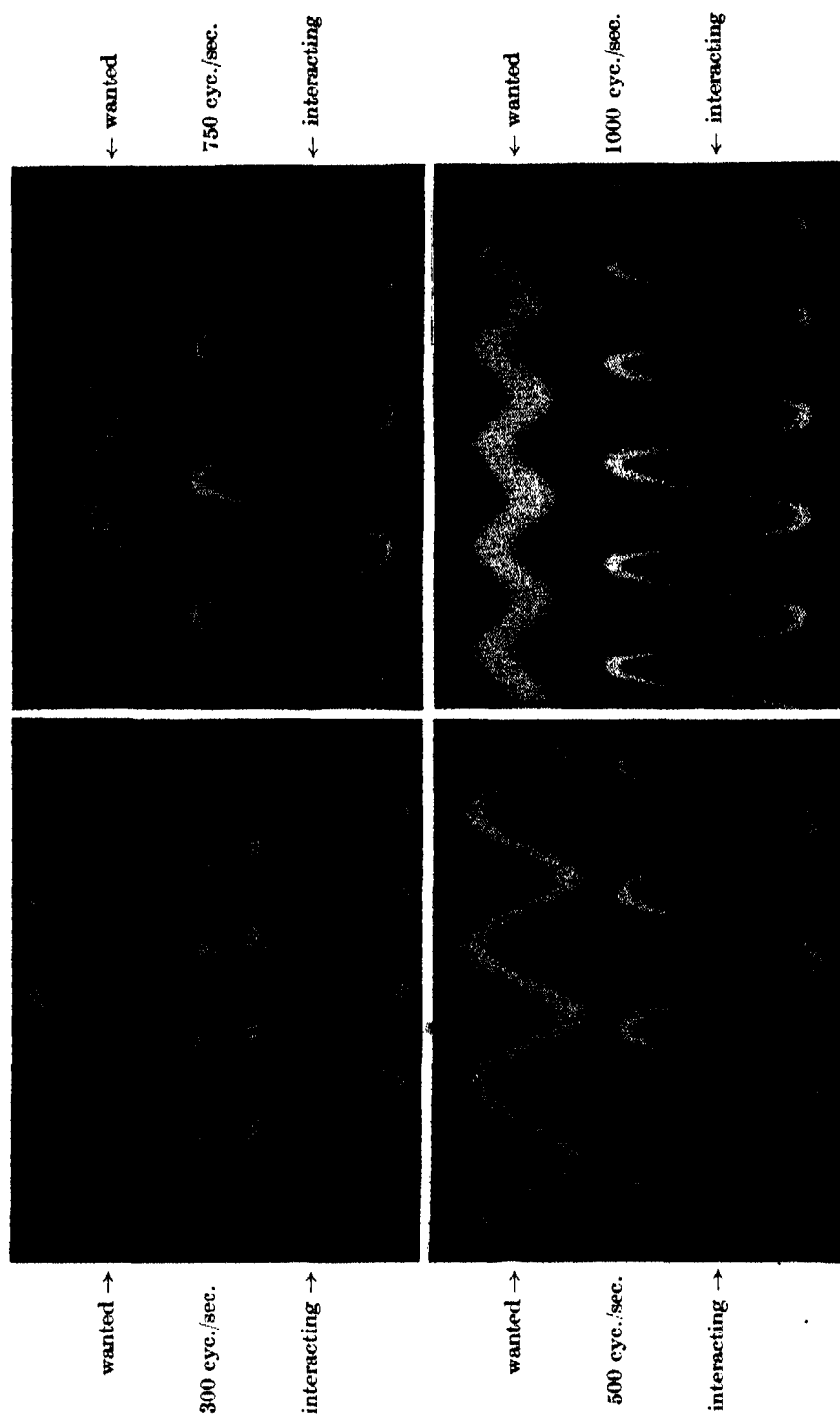


FIGURE 4. Records showing phase relation between the modulation received direct by the interacting wave, and indirectly after being transferred to the wanted wave by the process of wave-interaction. There is a progressive shift of phase as the modulation frequency is increased.

so that any residual phase-shift would be the same in each. The outputs of the two amplifiers were applied to deflect the two traces of a Cossor double-beam cathode-ray oscilloscope and were viewed on a linear time-base synchronized to the modulation. The equipment was tested by the application of radio-frequency e.m.f.'s generated in local signal-generators, modulated from a common source, and the amplitude of the wave-trace on the oscilloscope was shown to be proportional to the modulation amplitude of the input and independent of the frequency. The two traces were shown to be in phase, and to remain in phase over the operational frequency range. Tests were also made to demonstrate that no interaction occurred between the two amplifiers, and possible interaction in the oscilloscope was guarded against.

The method of experimentation usually adopted was to arrange for the wanted wave to be unmodulated, and for the interacting wave, usually with a power of 100 or 150 kW, to be modulated to a depth of 80 % with a series of pure tones having the frequencies 50, 75, 100, 150, 200, 300, 400, 500, 750, 1000, 1250, 1500, 1750, 2000 cyc./sec., the whole sequence of operations occupying about half an hour. The traces on the oscilloscope were either observed visually, or photographed and afterwards measured up, and the phase difference at each frequency was determined. A good measure of the phase difference could usually be obtained on all frequencies less than about 1000 cyc./sec. Examples of the type of trace observed are shown in figure 4.

When the observed phase-difference was plotted against modulation frequency a curve of the type shown in figure 5 was obtained. This curve may be explained in terms of the ideas outlined in § 1 in the following way. We show in appendix A that, as a result of the finite 'relaxation time' τ of the ionospheric electrons, the transferred modulation at a frequency f has a phase-lag $\phi_1 = \tan^{-1}(2\pi f\tau)$. If, also, there is a difference d between the two paths IAR and $IBCR$ of figure 1, there is an additional phase-lag given by $\phi_2 = 2\pi fd/c$. The total phase-lag ϕ is then the sum of the 'electron phase-lag' ϕ_1 and the 'path phase-lag' ϕ_2 , so that

$$\phi = \tan^{-1}(2\pi f\tau) + 2\pi fd/c.$$

When a set of experimental points had been plotted as in figure 5 the constants τ and d were chosen so as to give a theoretical curve lying smoothly among the points. The curve in figure 5 is drawn for $\tau = 1.8 \times 10^{-3}$ sec. and $d = 222$ km. In figure 6 the 'path phase-lag' ϕ_2 appropriate to this distance has been subtracted from the experimentally observed phase-lags and the resulting 'observed' values of ϕ_1 plotted as points. The curve represents $\phi_1 = \tan^{-1}(2\pi f\tau)$ for $\tau = 1.8 \times 10^{-3}$ sec. and the accuracy with which the points fall on it provide a measure of the reliability of the deductions.

The composition of the downcoming wave was frequently investigated, during a night's observations, by arranging that pulses of duration about $100 \mu\text{sec.}$ were emitted from the wanted station and observed at the receiver on an oscilloscope with a time-base synchronized, by way of the national 'grid' system of electric supply, to the emission of the pulses. A measurement of the intervals between the

pulses sufficed to decide whether a given pulse was reflected from region E or region F but it was not usually possible to make measurements with sufficient accuracy to provide a reliable measure of the height of the reflexion; this is particularly the case because the difference of path between the different multiple reflexions arriving at oblique incidence is not very sensitive to variations of the height of reflexion. We have therefore usually assumed that reflexions from region E occurred at a height of 100 km. and those from region F at 250 km.; these represent average heights of

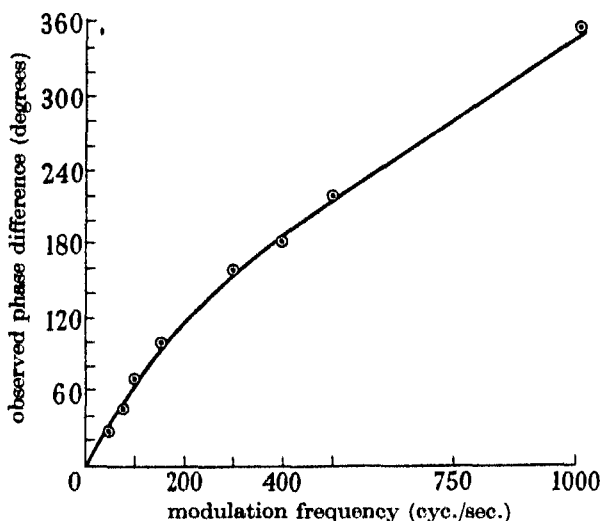


FIGURE 5. Experimental results obtained at 22.30 to 02.30 hr. G.M.T. on 4/5 May 1947, with Westerglen as wanted station and Ottringham as interacting station.

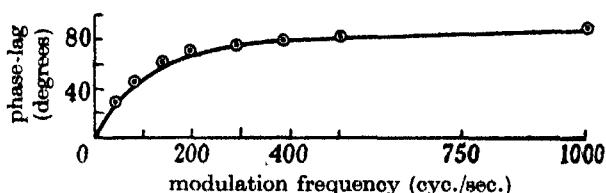


FIGURE 6. Curve of electron phase-lag against frequency. Experimental points marked $\odot$ are deduced from figure 5; the full line is the curve $\phi = \tan^{-1} (2\pi f \times 1.8 \times 10^{-8})$.

reflexion for waves of this frequency incident obliquely, as deduced from the routine ionospheric observations carried out at the Radio Research Station, Slough (lat. $00^{\circ} 45' W.$, long. $51^{\circ} 25' N.$).^{*} Our measurements of echo-patterns have fitted these values quite well. Comparison of successive reflexions from the same region also provided a measure of the absorption; this information will be used in the discussion contained in § 7.

^{*} We are much indebted to Dr R. L. Smith-Rose for supplying us with detailed information for the occasions of our experiments.

Some observations of the pulse transmissions have been made in the presence of a modulated interacting wave and the modulation transferred to one single reflected pulse, generally the first from region E, has been observed. It is probable that useful information could be derived from further observations made in this way.

In the theoretical interpretation of the curves of figures 5 and 6 we have assumed that there is one predominant downcoming wave from the wanted station and that all the interaction occurs at one point on its trajectory. The more complicated situation arising if these assumptions do not hold is analyzed in appendix B. On some occasions we have noticed that the phase of the transferred modulation alters during the 2 min. period of the observation; this is explained in the appendix as being due to the presence of two downcoming waves comparable in intensity. In general, however, the phase was constant during a period of observation, as we should be led to expect from the pulse transmissions which usually showed the first echo to be much stronger than the others.

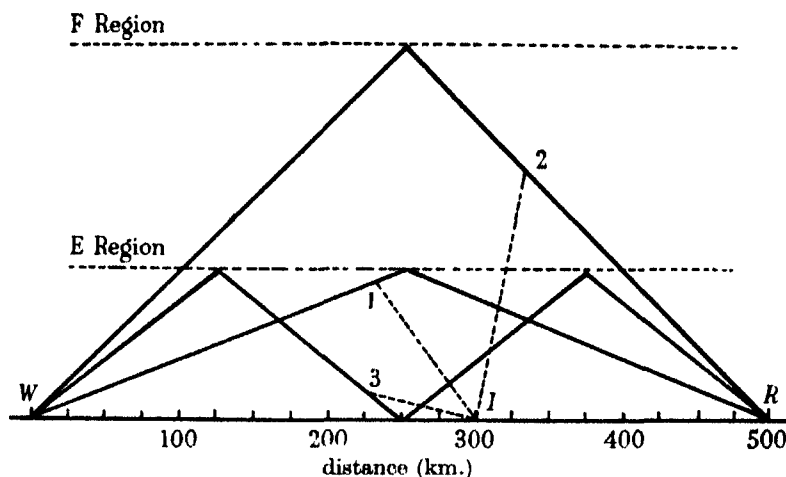


FIGURE 7. Possible locations of wave-interaction deduced from experiments, summarized in figures 5 and 6, which give an average path difference of 200 km.

From curves such as that of figure 5 the path difference d was deduced, and since the distance IAR in figure 1 was known, the distance $IBCR$ was calculated. Let us call this distance x . A series of possible wave-trajectories from the wanted station to the receiver was then drawn, as indicated in figure 7, and points (such as 1, 2, 3) on these trajectories were found which gave the measured value of x . The points marked in figure 7 correspond to the experimental results summarized in figure 5, in which Westerglen was used as the wanted station and Ottringham as the interacting station. In choosing amongst these possible positions for the origin of the wave-interaction we are now guided by the expectation that the interaction will be greatest where there is the greatest amount of absorption common to the two waves, and this region is just below the point of reflexion in region E. In the case illustrated in figure 7 we therefore select the point 1 as the probable location of the interaction.

Two series of experiments of the type outlined above have been carried out with the object of locating the region where the interaction occurs. In the first series the wanted wave was transmitted from Westerglen and the interacting wave from Ottringham. The results are summarized in table 2 and figure 8. In the second series the wanted wave was transmitted from Lisnagarvey and the interacting wave from

TABLE 2. RESULTS OF EXPERIMENTS IN WHICH WESTERGLLEN SENT THE WANTED WAVE AND OTTRINGHAM SENT THE INTERACTING WAVE

number of experiment	date (1947)	time (G.M.T.)	height of interaction region (km.)	value of $G\nu (=1/\tau)$ from phase curves (sec. ⁻¹)	value of $G\nu (=1/\tau)$ from amplitude curves (sec. ⁻¹)
1	10 January	01.00-02.30	95	623	725*
2	11 January	01.00-02.30	95	895	
3	4/5 May	22.30-00.30	90	555	
4	5/6 May	22.30-00.30	85	1260	

* Average for two nights.

TABLE 3a. RESULTS OF EXPERIMENTS IN WHICH LISNAGARVEY SENT THE WANTED WAVE AND DROITWICH (200 KCYC./SEC.) SENT THE INTERACTING WAVE

number of experiment	date (1947)	time (G.M.T.)	height of interaction region (km.)	value of $G\nu (=1/\tau)$ from phase curves (sec. ⁻¹)	value of $G\nu (=1/\tau)$ from amplitude curves (sec. ⁻¹)
5	15/16 June	22.30-02.30	77.5	2520	1640†
6	16/17 June	22.30-02.30	83.5	1640	
7	17/18 June	22.30-02.30	75.0	1260	—
8	3/4 July	22.30-02.30	91.5	1320	—
9	4/5 July	22.30-02.30	97.0	2890	—
10	5/6 July	22.30-02.30	78.0	1290	—
11	6/7 July	22.30-02.30	87.0	1010	—
12	6 August	23.00-23.30	84.0	890	—
13	7 August	00.10-00.30	80.0	720	—

† Average for three nights.

TABLE 3b. RESULTS OF EXPERIMENTS IN WHICH LISNAGARVEY SENT THE WANTED WAVE AND OTTRINGHAM THE INTERACTING WAVE

number of experiment	date (1947)	time (G.M.T.)	height of interaction region (km.)	value of $G\nu (=1/\tau)$ from phase curves (sec. ⁻¹)	value of $G\nu (=1/\tau)$ from amplitude curves (sec. ⁻¹)
14	15/16 June	22.30-02.30	85	—	—
15	16/17 June	22.30-02.30	92	1570	—

Droitwich or Ottringham. The results are summarized in table 3 and figure 9. In tables 2 and 3 the results of experiments are expressed in terms of the quantity $1/\tau$, since it is shown, in equation (21) of appendix A, that this is equal to the theoretically important quantity $G\nu$.

In the first series of experiments the interacting station was nearly on the straight line joining the receiver and the wanted station, in the second series the interacting station was some considerable distance from this line and the appropriate solid geometry had to be taken into account in calculating the location of the interaction.

The results of the phase measurements, as summarized in tables 2 and 3 and figures 8 and 9, are discussed in § 7.

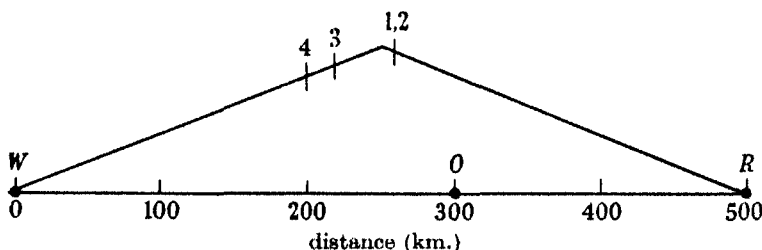


FIGURE 8. Locations of observed interaction of Ottringham on Westerglen (see table 2).

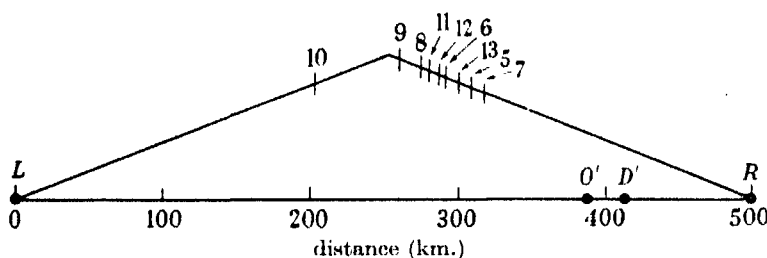


FIGURE 9. Locations of observed interaction of Ottringham and Droitwich on Lisnagarvey (see tables 3a and 3b). The points O' and D' represent the feet of the perpendiculars from Ottringham and Droitwich to the line joining Lisnagarvey and Cambridge.

5. MAGNITUDE OF THE INTERACTION

In order to measure the relative magnitude of the transferred modulation, a simple method was devised which gave good results even with a wave which exhibited marked fading. It was arranged that the wanted wave was weakly modulated with an amplitude of 5 or 10 % at a frequency somewhat different from the modulation frequency of the interacting station, so that, at the receiver, the normal modulation of the station was observable in addition to the modulation imposed by interaction. The trace on the oscilloscope then took the form shown in figure 10, in which the distance AB corresponds to the directly-impressed modulation and the distance CD to the transferred modulation. From oscillograms of this kind it was a simple matter to deduce the percentage modulation due to interaction. Although the

percentage of direct modulation as observed at the receiver changed, due to interference effects between different reflected waves, and although the amount of interaction also varied as the wave faded, it was found that the mean readings taken in this way were fairly constant and appeared to be reliable. They also agreed with direct measurements made by recording simultaneously the rectified current, which gave a measure of the carrier intensity, and the amplitude of the oscilloscope trace, and then calibrating with a modulated e.m.f. from a signal generator. Measurements made in this way led to the results described in the following sub-sections.

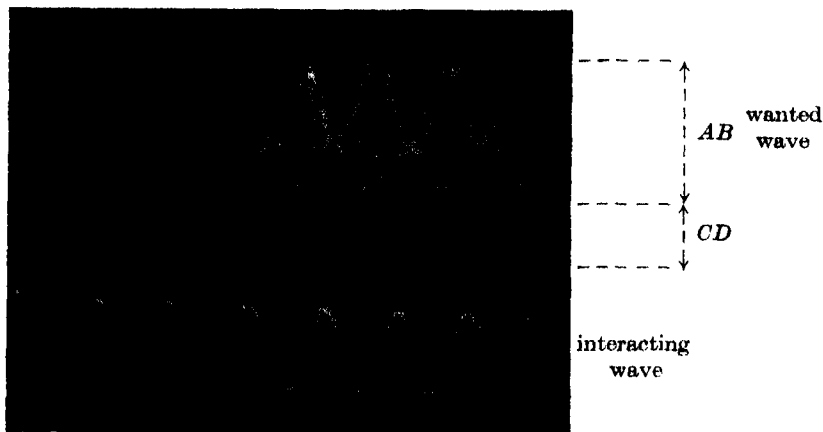


FIGURE 10. Photograph of oscilloscope trace to illustrate the method of measuring small amplitudes of interaction-modulation. The distance AB corresponds to 5% direct modulation at 500 cyc./sec. on the wanted carrier from Lisnagarvey and the distance CD to the transferred modulation. The interacting station was Droitwich (200 kcyc./sec.) modulated at 100 cyc./sec.

(a) *Magnitude of interaction as a function of modulation frequency*

The results of a typical series of measurements made as the modulation frequency was varied are shown in figure 11 and are similar to those obtained previously by other workers (van der Pol & van der Mark 1935; Huxley *et al.* 1947).

Equation (20a) of appendix A shows that we should expect the coefficient of modulation (m) superimposed on the wanted wave to be given by the expression

$$m = T \{ 2\mu / (1 + \frac{1}{2}\mu^2) \} \{ 1 + 4\pi^2 f^2 \tau^2 \}^{-1/2}. \quad (20a)$$

In this expression T is the 'coefficient of transferred absorption' defined by equation (8) of § 6; μ is the coefficient of modulation of the interacting wave modulated at frequency f ; and τ is the relaxation time of the ionospheric electrons.

That the experimental points plotted in figure 11 show a reasonable agreement with theory is seen by comparing them with the theoretical curve which has been plotted for $\tau = 5.8 \times 10^{-4}$ sec. On all occasions when the intensity of the interaction has been determined as a function of frequency in this way the agreement with

theory has been similar to that shown in figure 11 and the values obtained for the relaxation time τ are shown in tables 2 and 3. These values are discussed in § 7. An examination of all our results shows that the agreement with theory is not so good in the case of amplitude measurements as it is in the case of phase measurements. This difference, which may be seen by comparing figure 11 with figures 5 and 6, is difficult to explain.

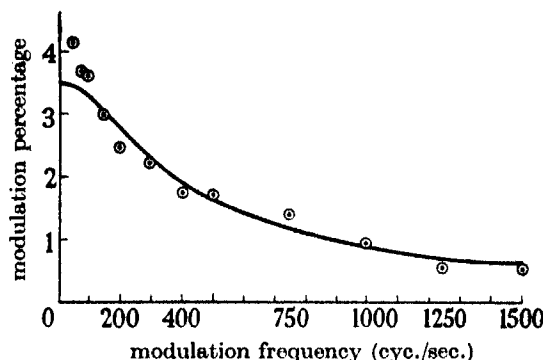


FIGURE 11. Percentage transferred modulation as a function of modulating frequency. Results obtained on 16/17 June, with Lisnagarvey sending the wanted wave and Droitwich the interacting wave. Experimental points $\odot$; full curve theoretical values for $\tau = 5.8 \times 10^{-4}$ sec.

If, in a plot such as that of figure 11, the curve showing best theoretical fit is extrapolated to zero frequency we obtain a value for the quantity $T\{2\mu/(1 + \frac{1}{2}\mu^2)\}$ and hence, since μ is known, for T . It has been confirmed that the value of T obtained in this way is in good agreement with the value obtained from measurements in which the unmodulated interacting carrier was switched on and off (see § 3).

We have made enough measurements of modulation amplitude as a function of modulation frequency to satisfy ourselves that the results are approximately represented by equation (20a) and we shall usually express the absolute magnitude of the interaction effect by stating the value of the 'coefficient of transferred absorption', T , deduced from curves of the type shown in figure 11, or measured directly by switching the interacting station on and off.

(b) *Coefficient of transferred absorption as a function of the power of the interacting station*

The theory of Bailey & Martyn (1934b) would lead to the expectation that the 'coefficient of transferred absorption' should be proportional to the radiated power of the interacting transmitter, but some tests by Grosskopf (1938) did not, apparently, confirm this expectation. We therefore conducted a special experiment in which the interacting wave was emitted from Ottringham and was modulated at a constant frequency of 400 cyc./sec. and the modulation impressed on a wanted wave emitted by Westerglen was measured, by the method described above, for different powers

of the interacting transmitter. The results are shown in figure 12 and appear to agree well with the theoretical expectation, in contrast with the results of Grosskopf. We have little doubt that the facts are in agreement with theory in this respect, but cannot suggest why the other workers found a different result.

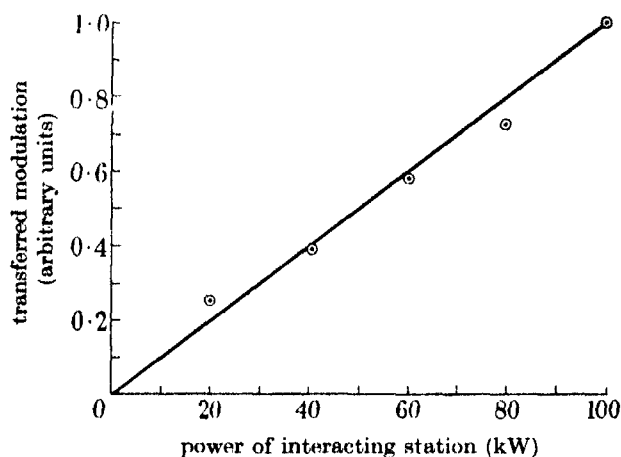


FIGURE 12. Results of varying the power of the interacting station, obtained at 00.30 hr. G.M.T. on 5 to 9 May, with Westerglen sending the wanted wave and Ottringham the interacting.

TABLE 4. OBSERVED VALUES OF COEFFICIENTS OF TRANSFERRED ABSORPTION

serial number	sender of wanted wave			sender of interacting wave			coefficient of transferred absorption		method of observation
	symbol on figure 2	frequency (keyc./sec.)	power (kW)	symbol on figure 2	frequency (keyc./sec.)	power (kW)	observed	reduced to 100 kW, 150 km.	
1	W	767	60	O	167	167	0.08	0.05	modulation and keying
2	W	767	60	GYA2	90.2	20	< 0.001	< 0.005	keying
3	L	1050	100	D(200)	200	170	0.04	0.023	modulation
4	L	1050	100	D(1013)	1013	60	0.03	0.029	modulation
5	L	1050	100	GBY	68	80	< 0.001	< 0.002	keying and modulation
6	L	1050	100	O	167	167	0.01	0.011	modulation
7	D(200)	200	170	D(1013)	1013	60	0.02	0.024	modulation*
8	D(1013)	1013	60	D(200)	200	170	0.04	0.029	modulation*
9	D(200)	200	170	O	167	167	0.04	0.029	modulation*
10	O	167	167	(D200)	200	170	0.02	0.014	modulation*

* Loop: ground ray suppressed.

(c) *Coefficient of transferred absorption with different pairs of stations*

An attempt was made to measure the 'coefficient of transferred absorption' with different pairs of sending stations to investigate in detail the effect of the radio frequencies and geographical positions of the senders. The powers of the interacting stations were not the same, and in order to reduce the results to a common basis for comparison the measured coefficients were expressed, by using the results of sub-section (b), in terms of an interacting transmitter of power 100 kW, distant 150 km. from the point of interaction. We shall refer to these modified coefficients as 'equivalent coefficients of transferred absorption'. The results obtained are shown in table 4.

Most of the measurements were straightforward and were made by the methods described in previous paragraphs. In one or two cases, however, special arrangements were used; thus when the morse station GYA2 was used as sender of the interacting wave it was not possible to modulate it and the tests had to be made by keying it on and off. The station GBY is constructed for single sideband telephony and the tests in which it emitted the interacting wave were made in two different ways. In one an audio-frequency tone was injected into the speech circuit and was keyed on and off; this produced an intermittent sideband at one frequency which simulated a keyed C.W. signal. In the other method the audio tone was itself modulated at 50 cyc./sec. so that the single sideband emitted was effectively a single carrier modulated at 50 cyc./sec.

The ultimate sensitivity of observation was set by the random noise received and when no interaction was observed an upper limit is given in table 4. The arrangement could have been made more sensitive by the use of narrow-band audio filters and it is proposed to use this method in future work.

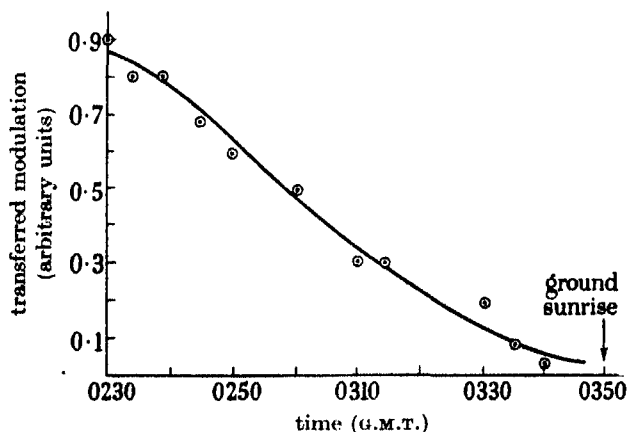


FIGURE 13. Decrease of interaction as dawn advances. Results of 7 July, with Lisnagarvey sending the wanted wave and Droitwich the interacting. Sunrise in the ionosphere at 100 km. was at 02.30 hr. G.M.T.

(d) The effect of sunrise on the coefficient of transferred absorption

It is well known that the intensity of downcoming waves decreases near sunrise due to increased absorption, and it is of interest to measure the coefficient of transferred absorption throughout this period. Experiments were made with Lisnagarvey as wanted station and Droitwich (200 kcy./sec.) as interacting station during the sunrise period on 7 July 1947.* The wanted station was modulated to a depth of 10 % (or sometimes 5 %) and the comparison method previously outlined was used. The results are shown in figure 13 from which it can be seen that the coefficient of transferred absorption was greatest during the night and became unmeasurably small during the hour before ground sunrise.

6. THEORETICAL CONSIDERATIONS

We shall now consider, in the light of present-day theories of absorption, the relation between interaction phenomena and the absorption of waves passing through the ionosphere. We shall calculate the magnitude of interaction effects in two parts. In the first part, contained in this section, we shall calculate the interaction effect at zero modulation frequency (corresponding to the switching on and off of the interacting wave), and shall express it in terms of a coefficient of transferred absorption (T), which we have already defined. In the calculations we shall refer to our ideas about the absorption of waves, so that our calculations, although allied to those of Bailey & Martyn, will be expressed somewhat differently. The second part of the calculation concerns the effect of the modulation frequency and is exactly that previously given by Bailey & Martyn. For the sake of completeness it is included, with our terminology, in appendix A.

We shall use the following nomenclature, in which we adhere to that used by Appleton in his theories of the ionosphere:

- c = velocity of light.
- e = electronic charge.
- f = modulation frequency.
- F = amplitude of received wave.
- F_0 = amplitude of received wave in absence of attenuation.
- ΔF = decrease in amplitude of received wave.
- G = proportion of energy lost by an electron in a collision.
- k = Boltzmann's constant.
- l = mean free path of electron.
- m = mass of the electron.
- N = number of electrons per c.c.
- p = angular frequency of the carrier.

* The exigencies of the broadcasting service, in conjunction with the use of Double British Summer Time, rendered it impossible to do these experiments except near midsummer.

$p_L = H_L e/mc$ = angular gyro-frequency of electrons in the longitudinal component of the earth's magnetic field.

$p_T = H_T e/mc$ = angular gyro-frequency of electrons in the transverse component of the earth's magnetic field.

P = power per unit area in the wave.

T = absolute temperature.

u = velocity of the electron.

U = gas-kinetic energy of the electron.

ΔU = increase in gas kinetic energy in presence of wave.

W = work done by the wave on each electron per second.

x = distance along wave normal.

α = a constant given by relation $\alpha\nu = \rho$.

ϵ_0 = permittivity of free space.

κ = absorption coefficient of wave per unit path.

ν = frequency of collision of electrons with molecules.

$\Delta\nu$ = change in collision frequency due to incident field.

ρ = attenuation of wave in 'nepers'.

(a) *The magnitude of wave-interaction*

The theory of ionospheric absorption is considerably complicated by the presence of the earth's magnetic field, and for simplicity we first consider what would happen in the absence of that field. Investigations of absorption of radio waves in the ionosphere (Farmer & Ratcliffe 1935) have led to the view that the waves are most strongly absorbed at a level where the refractive index does not depart much from unity, and that then the absorption coefficient is given by:

$$\kappa = \{2\pi N e^2 / \epsilon_0 cm\} \{\nu / (p^2 + \nu^2)\}. \quad (1)$$

There are also reasons for thinking that all the important absorption occurs at levels where $p^2 \gg \nu^2$ so that we may write approximately

$$\kappa = \{2\pi N e^2 / \epsilon_0 cm\} \{\nu / p^2\}. \quad (2)$$

As it travels through the ionosphere the interacting wave is absorbed at each level as given by this expression, and the power lost by it represents a 'heating up' of the ionospheric electrons and an increase in their velocity. If P represents the power per unit area in the wave at any given level in the ionosphere, then it is absorbed near that level according to the law $P = P_0 e^{-2\kappa x}$ so that the power absorbed in a slab of unit cross-section and of thickness dx is given by

$$-\frac{dP}{dx} dx = 2\kappa P dx.$$

But this slab contains $N dx$ electrons, so that the work (W) done per second on each electron is given by

$$W = 2\kappa P/N,$$

and substitution from equation (2) gives us

$$W = (4\pi e^2/\epsilon_0 mc)(\nu/p^2)P. \quad (3)$$

This work increases the gas-kinetic energy of the electron from the value U , which is in equilibrium with the gas molecules, to the value $U + \Delta U$. It is known from theory and from laboratory experiments that the average energy lost per collision by an electron under these conditions is proportional to its *excess* energy, and can be represented by $G\Delta U$ where G is a constant which has been estimated by Townsend and his school from experiments on the diffusion of slow electrons in gases (Townsend 1925). When equilibrium conditions have been set up under the application of a steady wave we can therefore express the fact that the work done on each electron per second is equal to the energy lost in the ν collisions made per second by writing

$$W = \nu G \Delta U. \quad (4)$$

We now wish to express energies in terms of collisional frequencies, so we relate the electron's velocity u to its collisional frequency ν and its mean free path l by the expression $u = \nu l$. We then have $U = \frac{1}{2}mu^2 = \frac{1}{2}ml^2\nu^2$ and $\Delta U = ml^2\nu\Delta\nu$ where $\Delta\nu$ represents the increase of ν due to the interacting wave. Substitution in equation (4) leads to

$$\Delta\nu = W/ml^2\nu^2G. \quad (5)$$

We now consider the passage of the wanted wave through the region which has been 'heated up' by the interacting wave. At each level in the ionosphere the absorption coefficient of the wanted wave is given by equation (2) and, if we assume that all the important absorption occurs near a fixed level, so that ν is roughly constant over the absorbing region, we may write, for the received amplitude of the wanted wave,

$$F = F_0 e^{-\rho} = F_0 e^{-\alpha\nu}, \quad (6)$$

where ρ represents the attenuation of the wave measured in 'nepers' and $\alpha\nu = \rho$. If now the presence of an interacting wave increases the frequency of collision from ν to $\nu + \Delta\nu$, the received amplitude is reduced to the value

$$F' = F_0 e^{-\alpha(\nu + \Delta\nu)},$$

and, if $\alpha\Delta\nu \ll 1$ we may expand the factor $e^{-\alpha\Delta\nu}$ and obtain

$$F' = F_0 e^{-\alpha\nu}(1 - \alpha\Delta\nu) = F(1 - \alpha\Delta\nu).$$

If ΔF represents the decrease in the amplitude, F , of the wanted wave we therefore have

$$\Delta F/F = \alpha\Delta\nu, \quad (7)$$

or, after substitution from equations (3) and (5),

$$T = \Delta F/F = \alpha(4\pi e^2/\epsilon_0 cm^2)(P/p^2)(l^2 G \nu)^{-1}. \quad (8)$$

We shall call the quantity $\Delta F/F$ the 'coefficient of transferred absorption' and shall write it as T . It represents the magnitude of the interaction effect at zero frequency. It is shown in appendix A that the coefficient (m) of modulation transferred from the interacting to the wanted wave at modulation frequency f is given by

$$m = T \{2\mu/(1 + \frac{1}{2}\mu^2)\} \{1 + 4\pi^2 f^2 \tau^2\}^{-\frac{1}{2}}, \quad (20a)$$

where μ is the coefficient of modulation of the interacting wave and τ is the relaxation time of the ionospheric electrons.

It will sometimes be more convenient to substitute for α from equation (6) and write the fractional decrease of amplitude in the form

$$T = \Delta F/F = (\rho/\nu) (4\pi e^2/\epsilon_0 cm^2) (P/p^2) (l^2 G\nu)^{-1}. \quad (9)$$

Another useful form of this expression containing the electron's velocity u is obtained by using the relation $u = \nu l$ and we then obtain

$$T = \Delta F/F = \rho (4\pi e^2/\epsilon_0 cm^2) (P/p^2) (Gu^2)^{-1}, \quad (10)$$

or, with $\frac{1}{2}mu^2 = \frac{3}{2}kT$

$$T = \Delta F/F = \rho (4\pi e^2/\epsilon_0 cm) (P/p^2) (3GkT)^{-1}. \quad (11)$$

Equation (7) may be rewritten

$$\Delta F/F = \alpha \Delta\nu = \rho \Delta\nu/\nu.$$

Measurement shows that when the interacting wave has a frequency of 200 kcy./sec. and comes from a 100 kW sender at a distance of 150 km. $\Delta F/F$ is of the order of 0.05 and with $\rho = 3$ we find $\Delta\nu/\nu$ is of the order 0.01. Hence the incidence of such a wave on the ionosphere increases the collisional frequency by about 1%. It follows that the effective temperature of the electrons increases by about 2% when this wave is incident.

(b) *Effect of earth's magnetic field*

To include the effect of the earth's magnetic field in the calculations is, in general, complicated, but the salient points can be seen simply in terms of Appleton's (1932) well-known magneto-ionic theory. The most important modification is to the absorption coefficient of the interacting wave as given by equation (2). This takes two forms according as the 'quasi-longitudinal' or the 'quasi-transverse' approximation (Booker 1935) is made, and for each approximation we have to consider separately the absorption of the 'ordinary' and the 'extraordinary' wave of the magneto-ionic theory. The results of this consideration are shown in table 5, which lists factors which replace p^{-2} in equation (2) when the magnetic field is included.

We first note that, for all directions of transmission, the extraordinary wave is strongly absorbed near the gyro-frequency ($p = p_L$ or p_H) so that we should expect to find a marked increase in the magnitude of wave-interaction when the frequency of the interacting wave approaches this value. Bailey (1937 *a, b* and *c*) has previously

discussed this phenomenon theoretically and observed it experimentally, and has named it 'gyro-interaction'. We are not further concerned with gyro-interaction in this paper.

We next note, from table 5, that as the frequency p of the interacting wave is decreased, the factor increases until, for cases (b), (c) and (e), p is somewhat less than the gyro-frequency, and then tends to a limiting value determined by the magnitude of p_L or p_T , or, roughly, the magnitude of p_H . In the case, however, of the ordinary wave travelling in a direction which satisfies the quasi-transverse approximations (case (d)), the factor, and therefore the magnitude of the wave-interaction, continues to increase as the frequency is decreased. We should therefore expect to find the magnitude of the interaction produced by a low-frequency wave to depend on the direction of propagation of that wave.

TABLE 5. FACTOR TO REPLACE THE FACTOR p^{-2} IN EQUATION (2)

approximation	factor
(a) no steady magnetic field	p^{-2}
(b) quasi-longitudinal—ordinary wave	$(p + p_L)^{-2}$
(c) quasi-longitudinal—extraordinary wave	$(p - p_L)^{-2}$
(d) quasi-transverse—ordinary wave	p^{-2}
(e) quasi-transverse—extraordinary wave	complicated expressions which can be shown to give a maximum absorption at the gyro-frequency, and for low frequencies to tend to p_T^{-2}

The results of this theoretical section as summarized in equations (8), (9), (10) and (11) which give the coefficient of transferred absorption in the absence of a magnetic field, and table 5, which gives the effect of introducing a magnetic field, will be used in the next section, to discuss the results of the measurements described in § 5.

7. DISCUSSION OF RESULTS

(a) *The determination of ν from $G\nu$*

We have previously given, in tables 2 and 3, the heights of the regions of interaction, and the measured values of the electronic relaxation time τ in these regions. It is shown in appendix A, equation (21), that $\tau = 1/G\nu$ so that as a result of the experiments the value of $G\nu$ is known at a known height, and if the value of G can be assumed ν can be determined. The best value of G , deduced from measurements in the laboratory, is taken by Bailey (1937a) to be 2.6×10^{-3} , and this, with the results of tables 2 and 3, gives values for ν ranging from 2.1×10^5 to 11×10^5 with a mean value $5 \times 10^5 \text{ sec.}^{-1}$. The measured heights of the interaction vary from 75 to 97 km. with a mean of 86.4 km. It is clear from the tables that there is considerable variation in the measured heights and relaxation times, and some of this variation

is undoubtedly due to experimental errors. A phase experiment of the type discussed in § 4 takes about 20 min. with the present technique, and since the complications discussed in appendix B undoubtedly occur we do not feel justified in drawing more than general conclusions from the results.

The broad conclusion, that ν has the value $5 \times 10^5 \text{ sec.}^{-1}$ at a level of about 85 km. is in good accord with other data. In particular it agrees with that previously found by Bailey (1935) who based his results on the measurements which van der Pol & van der Mark (1935) made on the amplitude of the transferred modulation.

(b) *Comparison of theoretical and experimental values
of the coefficients of transferred absorption*

The values of the 'equivalent coefficients of transferred absorption' calculated from equation (11), with suitable substitutions from table 5, are shown in table 6 together with the observed values extracted from table 4. The value taken for ρ in the calculations is derived from observations of the pulses emitted by the wanted station.

TABLE 6. EQUIVALENT COEFFICIENTS OF TRANSFERRED ABSORPTION FOR 100 kW SPHERICALLY RADIATED BY AN INTERACTING STATION DISTANT 150 KM. FROM THE POINT OF INTERACTION

Calculations are from equation (11) and table 5, with the following values inserted:

$\rho = 3$, corresponding to a reflexion coefficient of 0.05 for the wanted wave at oblique incidence.

$(2\pi c^2/\epsilon_0 cm) = 5.3 \times 10^{-2} \text{ cm.}^3 \text{ sec.}^{-2}$.

$P = 3.5 \times 10^{-4} \text{ ergs cm.}^{-2} \text{ sec.}^{-1}$ for 100 kW spherically radiated to a distance of 150 km.

$G = 2.6 \times 10^{-3}$.

$T = 200^\circ \text{ K.}$

$k = 1.37 \times 10^{-16} \text{ erg deg.}^{-1}$.

frequency of inter- acting wave (kcy.c./sec.)	calculated			observed values from table 4 (serial number of experiment in brackets)
	extraordinary quasi-longitudinal and approx. quasi-transverse	ordinary		
		quasi- longitudinal	quasi- transverse	
1013	1.4×10^{-1}	2.4×10^{-3}	1.3×10^{-2}	2.5×10^{-2} (4, 7)
200	1.1×10^{-2}	5.8×10^{-3}	3.3×10^{-1}	2.0×10^{-2} (1, 3, 6, 8, 9, 10)
90.2	8.7×10^{-3}	6.6×10^{-3}	1.6	$< 5 \times 10^{-3}$ (2)
68	8.4×10^{-3}	6.9×10^{-3}	2.8	$< 2 \times 10^{-3}$ (5)

In calculating from equation (11) we have assumed a knowledge of G and of the ionospheric temperature; we may, however, calculate from equation (9) and use the measured value of $G\nu$ so as to avoid any assumption about the value of G . We then have to assume reasonable values for ν and for the mean free path l and we obtain a result of the same order, as is indeed obvious if we remember that the measured value of $G\nu$ agrees with accepted values of G and ν .

In attempting to relate the observed and experimental results we first recall that, in the theoretical calculations of table 6, we have assumed that the interacting wave arrives at the region of interaction with its power undiminished; if it suffers appreciable absorption before it gets there the interaction will be less than that calculated.

We first consider the tabulated values of the coefficient of transferred absorption when the frequency of the interacting wave is 200 kcyc./sec. since this represents the case which we have studied in most detail in our experiments. We find that the calculated values lie on each side of the observed value and differ from it by a factor of less than 10. In view of the uncertainty concerning the precise magnitude of G this agreement seems satisfactory and we do not consider it profitable, at this stage, to consider further the absolute magnitude of the coefficient. We do, however, attach considerable significance to the relative magnitudes of the coefficient determined with interacting waves of different frequency, and shall examine these in more detail.

It is first interesting to note that the coefficient measured for experiment (1) of table 4 was about twice that measured in experiments (3), (6), (8), (9) and (10). This difference is probably attributable to the fact that, at the interaction point operative in the first experiment, the interacting wave was travelling more nearly transverse to the magnetic field, and its polarization corresponded to that of the 'ordinary' wave of the magneto-ionic theory.

We next examine the figures for the two low-frequency interacting waves and note that the observed coefficient of transferred modulation is less than 1/10 of that observed with an interacting wave of frequency 200 kcyc./sec. We can at once reject the possibility of interaction produced by an ordinary wave propagated with quasi-transverse direction since this would lead to an excessive amount of interaction. We next note that the calculated magnitudes of the interaction on this frequency for the other directions of transmission are very little different from those calculated for 200 kcyc./sec. We are driven to explain the much smaller observed interaction on the lower frequencies by the assumption that the full power of the interacting wave does not reach the region where the wanted wave is absorbed, either because the interacting wave is reflected or is considerably absorbed below this level.

In contrast to the case just considered it is next of special interest to inquire what interaction occurs between two waves on nearly the same frequency, which would be expected to be absorbed nearly at the same level in the ionosphere. Experiments numbers 4, 9 and 10 of table 4 are of this type, and the results listed in table 5 opposite the frequencies 1013 and 200 kcyc./sec. summarize the observations. For the frequency 1013 kcyc./sec. it is seen that the observed value is in good agreement with the theoretical values deduced both for the extraordinary wave and for the ordinary wave on the quasi-transverse assumption. On a frequency of 200 kcyc./sec. the possible theoretical values embrace a wider range but even so there is no disagreement between theory and experiment.

(c) The possibility of self-interaction

In the foregoing sub-section it has been emphasized that the maximum amount of interaction can only take place if the interacting and the wanted waves are absorbed in the same place, and the small interaction when the two wave-lengths have been different has been ascribed to the fact that the regions of absorption do not completely overlap. It is therefore of interest to inquire what would happen if the two wave-lengths were exactly the same and if they were travelling in the same direction so that the two absorption coefficients were identical at each point. The wanted and the interacting wave would then be one and the same, and the phenomenon could be called self-interaction. We believe that useful information could be obtained by measurements of self-interaction.

(d) Effects at sunrise

The coefficient of transferred absorption as given by equations (8), (9), (10) and (11), is dependent on the electron density N through the quantity ρ , which is the absorption coefficient of the wanted wave, and is proportional to N ; so that we might expect the coefficient of transferred absorption to increase as N increases with the approach of day, and as the absorption of the wanted wave increases. Grosskopf (1938) looked for an effect of this kind but did not observe it. In § 5(d) we have explained how we observed precisely the opposite effect, as illustrated in figure 13, and it is now necessary to consider how this could happen.

We first notice that, although the increase of electron density in a certain neighbourhood increases the total energy absorbed from the interacting wave it does not alter the work done on each electron by that wave (see equation (3)). So far as this effect goes, therefore, the coefficient of transferred absorption is not altered by an increase of electron density. If, however, the interacting wave is separately absorbed at some other level before it reaches the level where the interaction occurs then, of course, the power P in equation (3) is decreased, and, with it, the coefficient of transferred absorption. Separate absorption of the interacting wave at some other level *after* it has produced interaction does not alter the interaction in any way.

Turning now to consider the wanted wave, we have already noticed that an increase in its absorption in the region of interaction will increase the coefficient of transferred absorption. An increase of its absorption outside that region is simply equivalent to a decrease in the power emitted by the wanted sender and has no effect on the coefficient.

There are therefore two separate tendencies, acting in opposite senses:

(a) Increased absorption of the wanted wave in the region where interaction occurs leads to an increased coefficient of transferred absorption.

(b) Increased absorption of the interacting wave before it reaches the region of interaction leads to a decrease in the coefficient of transferred absorption.

Other changes of absorption do not alter the coefficient of transferred absorption.

We must conclude that, during the period of sunrise, phenomenon (b) more than compensates for phenomenon (a). A detailed discussion of the possibilities in the light of theories of ionospheric absorption should provide useful information about changes in the distribution of electron density during the period of sunrise.

8. CONCLUSIONS AND FUTURE EXPERIMENTS

We have shown that, if the magnitude of the quantity G is assumed, measurements of the phase of the transferred modulation lead to a knowledge of the frequency ν of collision between electrons and neutral molecules at a height which can be determined. Our measurements have shown that the value of ν is about $5 \times 10^8 \text{ sec.}^{-1}$ at a height of 85 km. They also indicate that this is the height at which the majority of the absorption occurs at night, and thereby confirm the suggestion that the main absorption does not occur at the top of the trajectory. In this respect our results differ from those of Bailey & Martyn (1934).

Measurements of the absolute magnitude of the transferred modulation during the night showed reasonable agreement with theory in the cases where the wanted and interacting waves were near the same frequency, e.g. experiments with serial numbers 4 (1 Mcyc./sec.) and 9 and 10 (200 kyc./sec.) (table 4). Since we expect the absorption of two waves of the same frequency to occur near the same level we take the agreement as providing additional evidence for the correctness of the assumed value for G and the value deduced for ν .

We also find reasonable agreement with theory when one wave has a frequency about 1 Mcyc./sec. and the other about 200 kyc./sec. (experiments 1, 3, 6, 7 and 8). This leads us to believe that the waves of these two frequencies are absorbed near the same levels during the night.

With interacting waves of frequencies 90 and 68 kyc./sec. the interaction is considerably less than would be expected and it appears that these waves must be reflected from heights less than 85 km., the level of absorption of the waves of higher frequency.

We deduce from the decrease of interaction observed when dawn approaches that the levels of absorption for 200 kyc./sec. and 1 Mcyc./sec. separate considerably, although they had been roughly coincident during the night. This is presumably due to the establishment during the dawn period of a less sharp gradient of ionization in the region of 85 km.

The measuring apparatus used in these experiments has intentionally been kept simple, and although well suited for establishing the main principles of the methods, suffered from the disadvantage that it required about half an hour to make a complete phase experiment. During this time ionospheric conditions may have changed so that no great accuracy is claimed for the values of $G\nu$ or of height given in tables 2 and 3. We intend to modify the apparatus so that measurements can be made while the modulation frequency is changed quickly.

In addition to those organizations whose help has been acknowledged in § 2, we wish to express our thanks to several others for help they have given. We wish to thank the Department of Scientific and Industrial Research which has supported the work with a generous grant. One of us (I. J. S.) is indebted to the Government of New Zealand for a scholarship which has enabled him to work in the Cavendish Laboratory on this subject. We are specially indebted to Mr S. W. H. W. Falloon for considerable help with the apparatus and with the observations, to Mr K. Weekes and Mr J. W. Findlay for help in the observations of the pulse transmissions, and to Dr L. G. H. Huxley for allowing us to see the results of some observations which he made at Birmingham on the transmissions described in this paper.

APPENDIX A

The magnitude of wave-interaction as a function of modulation frequency

In this appendix we extend the discussion of § 6 to include the case of a modulated interacting wave. The analysis was given in the original paper of Bailey & Martyn (1934*b*), we merely repeat it here in order to relate it to the nomenclature which we have used.

If there is a temporal variation in the power, $W(t)$, expended on each electron by the interacting wave, then the equation of energy balance (equation (4) of § 6 (*a*)) of the electrons becomes

$$W(t) = \frac{d}{dt}(\Delta U) + \nu G \Delta U, \quad (12)$$

or, if we substitute for ΔU in terms of $\Delta \nu$ as in § 6 (*a*):

$$W(t)/m l^2 \nu = \frac{d}{dt}(\Delta \nu) + \nu G \Delta \nu. \quad (13)$$

The power, $W(t)$, expended on each electron per second is related to the power-flux P in the interacting wave by the expression

$$W(t) = CP(t),$$

where

$$C = (4\pi e^2/\epsilon_0 mc)(\nu/p^2) \quad (14)$$

(cf. equation (3)) and we shall write

$$P(t) = P_0(1 + M \cos \omega t) \quad (15)$$

to represent a modulated wave.

If we now substitute from equations (14) and (15) into (13) and solve for $\Delta \nu$ we obtain

$$\Delta \nu = (CP_0/ml^2\nu^2G)[1 + M\{1 + (\omega/G\nu)^2\}^{-1} \cos(\omega t - \phi)], \quad (16)$$

where

$$\phi = \tan^{-1}(\omega/G\nu).$$

Substitution of this result into equation (7) together with expression (14) for C gives

$$\Delta F/F = \alpha(4\pi e^2/\epsilon_0 cm^2)(P_0/p^2)(l^2G\nu)^{-1}[1 + M\{1 + (\omega/G\nu)^2\}^{-1} \cos(\omega t - \phi)]. \quad (17)$$

If the wave *amplitude* is sinusoidally modulated with a coefficient μ there will be an octave component in the modulation of the *power*, but if this is neglected (as it was in our experiments) and we consider only the fundamental component we have

$$M = 2\mu/(1 + \frac{1}{2}\mu^2). \quad (18)$$

It should be noted that, although μ is always less than unity, M may be greater than unity. In our experiments, for example, μ was 0.8 and M was therefore 1.21.

If we combine expression (18) with expression (17) and substitute from equation (8) for the coefficient of transferred absorption T , we find that

$$\Delta F/F = T[1 + \{2\mu/(1 + \frac{1}{2}\mu^2)\}\{1 + (\omega/G\nu)^2\}^{-1} \cos(\omega t - \phi)]. \quad (19)$$

Equation (19) shows that, if $T \ll 1$ the wanted wave is modulated with a modulation coefficient m given by

$$m = T\{2\mu/(1 + \frac{1}{2}\mu^2)\}\{1 + (\omega/G\nu)^2\}^{-1}, \quad (20)$$

and the phase of this transferred modulation lags on that of the interacting modulation by the angle $\phi = \tan^{-1}(\omega/G\nu)$.

The quantity $1/G\nu$ plays an important part in the phenomena discussed in this appendix and it is of interest to give it a physical meaning. Reference to equation (12) shows that, if the interacting wave is suddenly removed the electrons will lose their excess energy ΔU as given by

$$\frac{d}{dt}(\Delta U) + \nu G \Delta U = 0,$$

or

$$\begin{aligned} \Delta U &= (\Delta U)_0 e^{-\nu G t} \\ &= (\Delta U)_0 e^{-t/\tau}, \end{aligned} \quad (21)$$

where $\tau = 1/G\nu$ can be called the 'relaxation time' of the electrons. We shall often use equation (20) written as

$$m = T\{2\mu/(1 + \frac{1}{2}\mu^2)\}\{1 + 4\pi^2 f^2 \tau^2\}^{-1}. \quad (20a)$$

APPENDIX B

Effects of transmission over multiple paths

In this appendix we consider how the following complicating processes will modify the amplitude and phase of the transferred modulation measured at the receiver:

(a) Two ionospheric waves reach the receiver by different paths and each has modulation transferred to it at some point along its trajectory. We shall restrict ourselves to the case where one of the waves is much weaker than the other.

(b) A single ionospheric wave has modulation transferred to it at two different points along its trajectory. We shall restrict ourselves to the case where one modulation is much weaker than the other.

(c) A single ionospheric wave with modulation transferred to it at a single point in its trajectory is received simultaneously with a ground wave which carries no transferred modulation.

We first consider case (a). Let us suppose that, as indicated in figure 14, down-coming waves from W are received at R simultaneously by way of reflexion from region E at the point E and from region F at the point F , and that interaction takes place on the two waves separately at the points B and C . Let the path differences for each wave separately be given by

$$ICFR - IAR = d_2, \quad IBER - IAR = d_1,$$

and let the amplitude of the two radio-frequency waves be A_1 and A_2 on arrival at R and their coefficients of transferred modulation be m_1 and m_2 . If then the angular

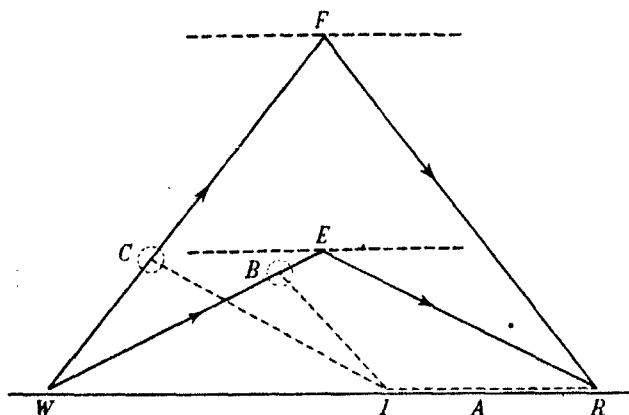


FIGURE 14. Schematic diagram to illustrate discussion of simultaneous reception of two downcoming waves each carrying transferred modulation.

radio-frequency is denoted by p and the angular audio-frequency by ω , the two waves produce e.m.f.s at the receiver given by

$$\left. \begin{aligned} A_1[1 + m_1 \cos \{\omega t - \omega d_1/c - \phi(\omega)\}] \cos pt, \\ A_2[1 + m_2 \cos \{\omega t - \omega d_2/c - \phi(\omega)\}] \cos (pt + \psi). \end{aligned} \right\} \quad (22)$$

and

In these expressions the phase of the modulation is referred to a zero which is the phase of the modulation on the wave received direct from I by the path IAR ; the phase angle $\phi(\omega)$ is given by $\tan \phi = \omega \tau$ and represents the phase-lag due to the effect of the electronic relaxation time in the ionosphere; and the phase angle ψ is included to represent the difference in the phase of the radio-frequency e.m.f.'s received by the two paths.

We first rewrite expressions (22) as

$$\left. \begin{aligned} A_1(1 + m_1 \cos \theta_1) \cos pt, \\ A_2(1 + m_2 \cos \theta_2) \cos (pt + \psi), \end{aligned} \right\} \quad \text{where} \quad \left\{ \begin{aligned} \theta_1 &= \omega t - \omega d_1/c - \phi(\omega), \\ \theta_2 &= \omega t - \omega d_2/c - \phi(\omega), \end{aligned} \right\} \quad (23)$$

and we then find for the resultant e.m.f. the expression

$$\left\{ \frac{A_1^2(1 + m_1 \cos \theta_1)^2 + A_2^2(1 + m_2 \cos \theta_2)^2}{+ 2A_1 A_2(1 + m_1 \cos \theta_1)(1 + m_2 \cos \theta_2) \cos \psi} \right\}^{\frac{1}{2}} \cos(pt + \chi), \quad (24)$$

where χ is a phase angle depending on the other variables. If we assume m_1 and $m_2 \ll 1$, the amplitude A of this resultant radio-frequency e.m.f. may now be expressed as

$$A = A_0 \left\{ 1 + \frac{(A_1/A_0)^2 m_1 \cos \theta_1 + (A_2/A_0)^2 m_2 \cos \theta_2}{+ (A_1 A_2/A_0^2)(m_1 \cos \theta_1 + m_2 \cos \theta_2) \cos \psi} \right\} \quad (25)$$

where

$$A_0^2 = A_1^2 + A_2^2 + 2A_1 A_2 \cos \psi.$$

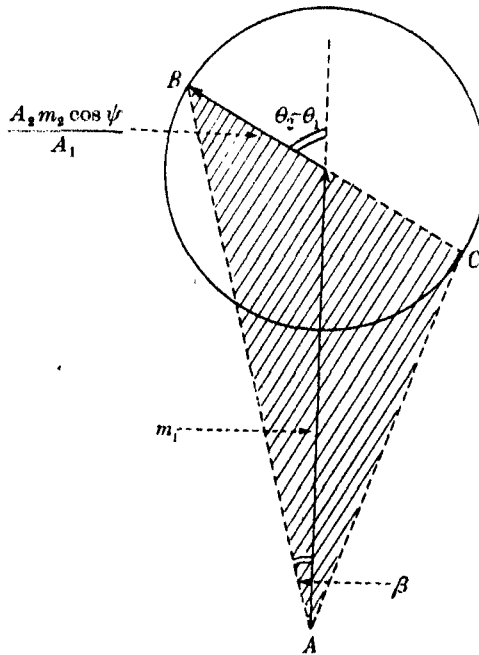


FIGURE 15. To illustrate meaning of equation (25).

The last three terms inside the bracket represent the modulation of the wave which, in general, may be quite complicated. In order to simplify matters we shall assume that A_2 is small compared with A_1 , so that the expression in the bracket reduces approximately to

$$1 + m_1 \cos \theta_1 + (A_2/A_1) m_2 \cos \psi \cos \theta_2. \quad (26)$$

The modulation then consists of two superimposed sinusoidal modulations with amplitudes m_1 and $(A_2/A_1) m_2 \cos \psi$ and with a phase difference given by

$$\theta_1 - \theta_2 = \omega(d_2 - d_1)/c.$$

The resultant of these two simultaneous modulations is most simply visualized by a vector diagram such as that of figure 15 in which the vectors are supposed to rotate with the frequency of the modulation. It is then clear that the phase of the resultant modulation will differ by the angle β from the phase of the modulation

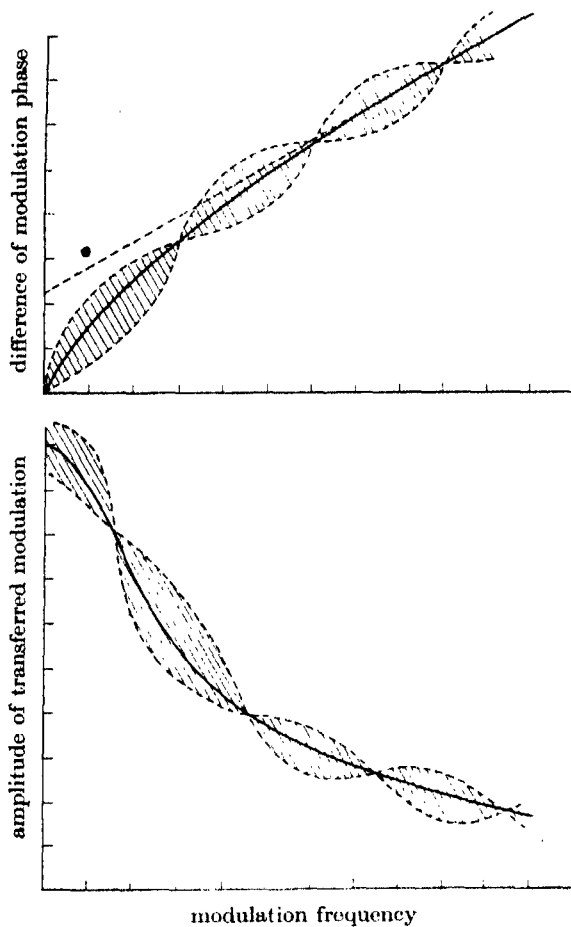


FIGURE 16. The expected effect of interaction on two simultaneously-received downcoming waves. The solid line represents the theory for interaction at one point on a single downcoming wave. For interaction on each of two downcoming waves the resulting curves lie somewhere inside the shaded regions, the precise position depending upon the radio-frequency phases of the two waves.

due to A_1 alone. The magnitude of this phase difference depends on the quantity $A_2 m_2 \cos \psi / A_1 m_1$ and on the phase difference $(\theta_1 - \theta_2)$ between the modulations received separately by the two paths. Small changes in the ionosphere will cause ψ to assume a series of random values and will lead to changes in A_1 and A_2 ; as these changes occur the amplitude and phase of the received modulation will assume

values represented by vectors in the shaded triangle ABC . In any experiments, therefore, there will be an element of random 'scatter' amongst a set of points plotted to represent the phase or amplitude of the modulation. If the modulation frequency is altered as the experiments proceed, the magnitude of $\theta_1 - \theta_2 = \omega(d_2 - d_1)/c$ will alter, and when $\theta_2 - \theta_1 = 0$ the variations of $A_2 m_2 \cos \psi / A_1 m_1$ will not affect the

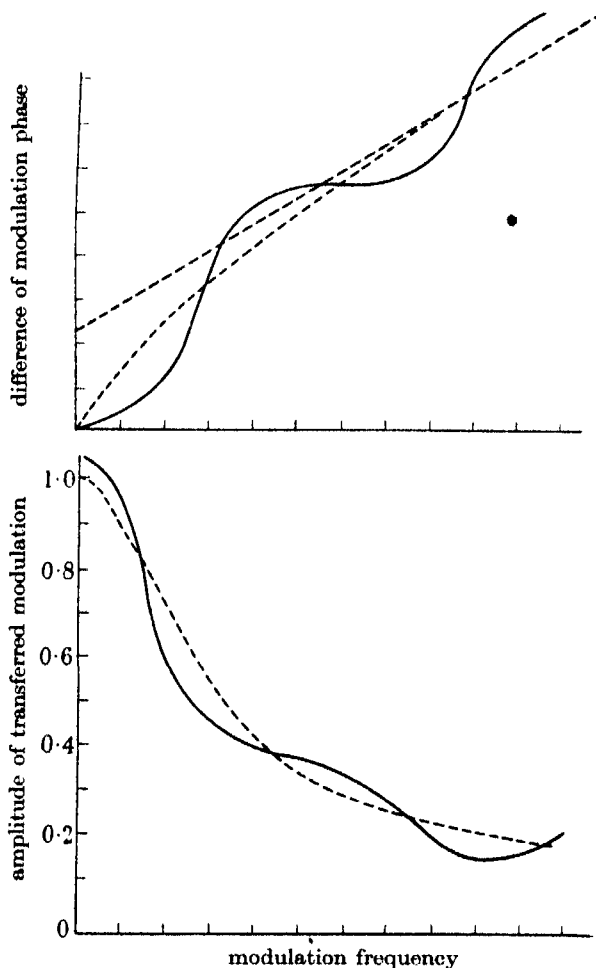


FIGURE 17. The expected effect of simultaneous interaction at two points on a single downcoming wave. The dotted lines represent the theory for interaction at one point, and the solid lines the results for interaction at two points.

phase of the resultant modulation but will have maximum effect on the amplitude, whereas when $\theta_2 - \theta_1 = \frac{1}{2}\pi$ there will be a marked effect on the phase, but little on the amplitude. If interaction occurred, in the ideally simple way, at one point on one ray, the theories which we have previously given would lead us to expect the plots of experimental results to fall on curves typified by the solid lines of figure 16.

The occurrence of interaction on two transmission paths, between which there was a variable phase, would cause the plots of experimental results to be scattered about these lines, in such a way as to lie always in the regions shown shaded.

To consider case (b), where a single ionospheric wave has modulation transferred to it at two different points along its trajectory, we use precisely the same analysis as before and put $A_1 = A_2$, $m_1 \gg m_2$, and keep ψ constant. If, now, A_2/A_1 also remained constant we should find our experimental points lying on a curve such as that of figure 17. There may be some scatter around this curve as a result of changes in the magnitude of A_2/A_1 .

We now consider case (c), where a single ionospheric wave, with modulation transferred to it at a single point in its trajectory, is received simultaneously with a ground wave which carries no transferred modulation. Our previous expressions represent this case if we take $A_1(=)A_2$ and $m_2 = 0$, and equation (25) then becomes

$$A = A_0[1 + \{(A_1/A_0)^2 + (A_1 A_2/A_0^2) \cos \psi\} m_1 \cos \theta_1].$$

This expression shows that the phase of the transferred modulation is not affected by the presence of the ground wave except that it may be completely reversed if $\cos \psi$ is negative and $|A_2 \cos \psi| > A_1$. It is important to remember this possibility when interpreting the absolute phase of the transferred modulation in the presence of a relatively strong ground wave received from the wanted transmitter.

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The excitation of nuclei by electrons

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The cross-section for the inelastic scattering of electrons by atomic nuclei is calculated assuming the process to arise from the electromagnetic interaction between electrons and protons. For fast electrons scattered by cadmium the cross-section so obtained is in fair agreement with recent experimental estimates. Difficulties, due to the failure of Born's approximation, arise when an attempt is made to apply the theory to the explanation of the electron excitation curves recently observed by Wiedenbeck.

1. INTRODUCTION

The purpose of this paper is to attempt the calculation of the cross-section of the inelastic scattering of electrons by nuclei. This process may be symbolically represented by the equation

$$e + (Z, A) \rightarrow e' + (Z, A)^*, \quad (1)$$

where e and e' denote the incoming and the scattered electrons respectively and (Z, A) denotes a nucleus of atomic weight A and atomic number Z . The asterisk denotes an excited state of the nucleus.

The process is assumed to arise from the electromagnetic interaction between the electron and the nuclear charge. For the determination of this cross-section we shall make use of the relativistically invariant theory of the retarded interaction of two charged particles developed by Möller (1931).

The only alternative interaction between electrons and nuclei capable of leading to a process of this kind is that derived on the basis of the Fermi theory of β -decay. Since in the Fermi theory the first order process corresponds to the transformation of an electron into a neutrino (charge is conserved by the simultaneous transformation of a proton into a neutron), inelastic scattering must be a second order process. For the mere excitation of nuclei, however, the first order process will already give a non-vanishing result. The cross-section of this process of approximately 10^{-40} cm.² is doubtlessly too small to account for the observed cross-sections for electronic excitation. The second order process, on the other hand, leads into the well known divergence difficulties (for energies for which the first order process is allowed). With a suitable cut-off procedure, however, the cross-section corresponding to the second order process may be estimated as 10^{-64} cm.² where the factor 10^{-24} against the first order process is due to the square of the 'fine structure constant' corresponding to the neutrino-theory.

The actual method applied for the calculation of the cross-section is based on the use of a formula derived by Bethe (1932) from the Möller theory. This derivation,

however, is based on Born's approximation method and thus restricts the applicability of its results to large energies of both incoming and outgoing electron and small atomic numbers.

In order to simplify the calculation it is necessary to expand the integrand of certain matrix elements in powers of the nuclear radius divided by the wave-length which corresponds to the change of momentum of the electron. This simplification, which has the advantage of allowing us to compute cross-sections in terms of known experimental data, as dipole and quadrupole moments, restricts the applicability of the theory to electron-energies below approximately 50 MeV for medium nuclei.

The analysis of this paper has been carried out for electric dipole, electric quadrupole and magnetic dipole transitions. In the case of the electric dipole the cross-section comes out to be given by equation (27) below. Apart from a trivial numerical discrepancy this formula is identical with that used by Mamasach'isov (1943) for the determination of the cross-section of the electronic disintegration of Be⁹.† The corresponding formulae for the cases of electric quadrupole and magnetic dipole transitions are equations (35) and (40) below. In all cases, the cross-section is a monotonic increasing function of the kinetic energy, as shown in figures 1 and 2.

This appears to be due to the assumption of vanishing nuclear charge necessary to safeguard the applicability of Born's approximation. The electrons are represented by plane Dirac waves and the influence of the central Coulomb field is neglected. This seems to be a good approximation for high energies but certainly fails near the threshold. This may be seen in the following way: The main contribution to the cross-sections comes from those parts of the incoming and outgoing electronic wave which are within a sphere with a radius equal to the wave-length corresponding to the change of momentum and the nucleus as centre. The wave function of the outgoing electron will be violently wrong within a sphere in which its kinetic energy due to the Coulomb attraction is equal or larger than its kinetic energy at infinity. The radius of this sphere is

$$r^* = \frac{e^2 Z}{E_{\text{kin.}}},$$

where $E_{\text{kin.}}$ is the kinetic energy of the electron, and the condition for the applicability of Born's approximation is $r^* \ll \lambda$, where λ is the wave-length corresponding to the change of momentum of the electron. The theory will, therefore, be unreliable in the region

$$E_{\text{kin.}} < \frac{1}{2\pi} \frac{Z}{137} cp,$$

where p is the momentum of the incoming electron corresponding to the excitation energy of the nucleus. For an atomic number in the neighbourhood of 50 and for $p \sim 3mc$ the critical kinetic energy is approximately 70 kV.

† This paper came to our knowledge after the publication of a recent letter to the editor of *Nature* (Touschek 1947).

This breakdown of the method of approximation is well known to be responsible for the interesting anomalies in the electron excitation curves of optical transitions (Massey & Mohr 1931). Its effect in this analogy is a very rapid increase in the excitation curve near the threshold leading to a maximum, the width of which is roughly determined by the wave-length of the scattered electron. In the optical case, however, the effect is complicated by exchange phenomena.

We do not attempt to calculate this feature of the excitation curves in the present paper. In the limit of low energies it would be a sufficiently good approximation to treat the nuclear transition as a point dipole or quadripole but a better treatment of the electron wave function would, of course, be required. We would merely point out that an increase of the cross-section as compared with that determined by Born's approximation is to be expected. Formulae (27), (35) and (40) have the common feature that the cross-section as a function of the energy of the scattered electron increases like $E_{\text{kin}}^{\frac{1}{2}}$. As an indication of the order of magnitude of the correction due to the effects of the Coulomb field around the nucleus we may multiply the cross-section by a Gamow factor

$$\frac{2\pi Z}{137\beta} \left(1 - \exp \left(-\frac{2\pi Z}{137\beta} \right) \right)^{-1},$$

where β is the velocity of the outgoing electron with c as unit. (This factor gives the value of the modulus of the wave function in a Coulomb field which asymptotically behaves like a plane wave with unit amplitude.) The influence of this correction is to make the excitation curve start with a constant value from the threshold, which under suitable conditions might lead to a peak of the excitation curve. We have indicated this possible behaviour of the curve by the dotted line in figure 1. It will be noticed that the width of the peak corresponds to the critical energy defined by the breakdown of the Born approximation.

The formulae for the cross-sections outside the critical region involve quantities which can be calculated readily by the use of the liquid-drop model of the nucleus. In this model the electric and magnetic dipole moments vanish and only quadrupole and higher electric transitions are possible. The cross-section for electron excitation of quadrupole transitions in cadmium calculated in this way is, however, roughly 200 to 2000 times larger than the value estimated experimentally, but the disagreement is not too serious when we consider the limitations inherent in the use of the liquid-drop model.

2. GENERAL THEORY

We wish to calculate the cross-section for the process described by equation (1). If we denote the energy of the incident electron by ϵmc^2 , where m is the mass of the electron, and that of the scattered electron by $\epsilon' mc^2$, then the conservation of energy gives

$$\epsilon = \epsilon' + \Delta + T, \quad (2)$$

where Δmc^2 is the excitation energy imparted to the nucleus and Tmc^2 is the energy of recoil of the nucleus. Similarly if $\mathbf{p}mc$, $\mathbf{p}'mc$ are the momenta of the incident and

scattered electrons and $km c$ is the momentum of the recoiling nucleus we obtain from the conservation of momentum the relation

$$\mathbf{p} = \mathbf{p}' + \mathbf{k}. \quad (3)$$

Now if MA is the mass of the nucleus the relation between the energy and momentum gives

$$T = mk^2/2MA \ll \Delta,$$

so that we may omit T in equation (2) as long as $|\mathbf{k}|$ is not too large. Physically this infers that the nucleus is capable of absorbing any amount of momentum without affecting the energy balance.

Bethe has calculated the cross-section for inelastic processes, which according to Möller's theory may be written in the form

$$d\phi = 2r_0^2 d\omega \frac{e e' p'}{p} (\Delta^2 - k^2)^{-2} \sum_{\sigma} \sum_{\sigma'} |\overline{P}|^2, \quad (4)$$

where $r_0 = 2.8 \times 10^{-13}$ cm. is the radius of the electron and $d\omega$ is the element of solid angle into which the electron is ejected after inelastic scattering. The quantity P is defined by the equation

$$P = \int [\rho \rho_e - (\mathbf{j} \cdot \mathbf{j}_e)] d\mathbf{r}, \quad (5)$$

where ρ and ρ_e are the transition densities of the scattering and the scattered particles (that is the protons and the electrons) and $\mathbf{j}$ and $\mathbf{j}_e$ are the corresponding currents measured with e as unit. The summations in equation (4) have to be carried out over the spins of the initial and final states of the electron, and $|\overline{P}|^2$ denotes the mean value of $|P|^2$ over all initial orientations of the nucleus. The factor 2 which occurs in equation (4) replaces Bethe's factor 4 which differs from that occurring in our notation because of the fact, that Bethe has to average over the spins of the final state whereas we sum over these spins in order to preserve a certain degree of symmetry between the incident and scattered electron.

Since the process under consideration is due to electrons passing fairly far outside the nucleus we may represent the electrons by plane waves, so that

$$\rho_e = u'^* u e^{i(\mathbf{k} \cdot \mathbf{r})} = a_0 e^{i(\mathbf{k} \cdot \mathbf{r})}, \quad \mathbf{j}_e = u'^* \boldsymbol{\alpha} u e^{i(\mathbf{k} \cdot \mathbf{r})} = \mathbf{a} e^{i(\mathbf{k} \cdot \mathbf{r})}. \quad (6)$$

In these equations u denotes the spin amplitude and $\boldsymbol{\alpha}$ is the vector formed by the Dirac operators $\alpha_x, \alpha_y, \alpha_z$. It should also be noted that the distance r is measured with the Compton wave-length ($137r_0$) as unit.

The calculation of the total cross-section may be divided into three parts: the calculation of the average over the orientation of the nucleus, the spin summations and finally the integration over the directions of $\mathbf{p}'$. In order to carry out the first two steps of the calculation we note that the quantities ρ and $\mathbf{j}$ are not independent of one another. If we write

$$\mathbf{J} = \int e^{i(\mathbf{k} \cdot \mathbf{r})} \mathbf{j} d\mathbf{r} \quad (7)$$

we may make use of the continuity equation

$$\operatorname{div} \mathbf{j} + \frac{\partial \rho}{\partial t} = 0$$

to express $\int \rho e^{i(\mathbf{k} \cdot \mathbf{r})} d\mathbf{r}$ in terms of $\mathbf{J}$. Considering that ρ has the time dependent factor $e^{i\Delta t}$, integrating the continuity equation throughout space after multiplication by $e^{i(\mathbf{k} \cdot \mathbf{r})}$, and making use of Gauss's theorem we obtain

$$\int \rho e^{i(\mathbf{k} \cdot \mathbf{r})} d\mathbf{r} = \frac{1}{\Delta} (\mathbf{k} \cdot \mathbf{J}). \quad (8)$$

Substituting from equation (8) into equations (6) and (5) we obtain

$$\Delta P = \{(a_0 \mathbf{k} - \Delta \mathbf{a}) \mathbf{J}\}, \quad (9)$$

where the product involved is a scalar product. Writing for simplicity

$$\mathbf{s}(\sigma, \sigma') = a_0 \mathbf{k} - \Delta \mathbf{a}_0 \quad (10)$$

and putting

$$\sum_{\sigma} \sum_{\sigma'} \mathbf{s}^* \mathbf{s} = S, \quad (11)$$

where now the product on the left-hand side of the equation is dyadic, we obtain from equation (9)

$$\Delta^2 \sum_{\sigma} \sum_{\sigma'} |P|^2 = (\mathbf{J}^* \cdot S \cdot \mathbf{J}). \quad (12)$$

It follows from its definition (11) that the quantity S is a Hermitian tensor in three-dimensional space, i.e. $S_{ij}^* = S_{ji}$. The evaluation of the tensor S is straightforward and will be carried out in the next section. The averaging over the initial orientations of the nucleus is a much more difficult problem; consequently we do not attempt to develop the general theory but instead restrict ourselves to certain simplified cases.

These simplifications arise in the usual way from the expansion of $e^{i(\mathbf{k} \cdot \mathbf{r})}$ in powers of $(\mathbf{k} \cdot \mathbf{r})$. The use of this expansion is equivalent to assuming that $(\mathbf{k} \cdot \mathbf{r}) \ll 1$ within the nucleus. This simplification restricts the applicability of our results to energies below 70 MeV. On the other hand it has the advantage of allowing us to relate cross-sections to other experimental data. The range beyond 70 MeV becomes accessible by the assumption of a free particle model for the nucleus; this is the procedure generally adopted when the de Broglie wave-length of the incident particle is comparable with the dimensions of the nucleus. In this range the excitation of the nucleus to discrete energy-levels is of less importance than processes involving the emission of a heavy particle from the nucleus. A special case of this type—the electronic disintegration of Be^9 with the emission of a neutron near the threshold of this process—has been considered by Mamasachlisov (1943). The general theory of such processes will be discussed in a later communication.

The special cases which we shall treat by this method are: (i) electric dipole transitions; (ii) electric quadrupole transitions; (iii) magnetic dipole transitions.

In the electric dipole case the vector $\mathbf{J}$ is defined by

$$\mathbf{J} = \int \mathbf{j}(\mathbf{r}) d\mathbf{r} \quad (13)$$

and in the cases of the electric quadrupole and magnetic dipole it is defined by

$$\mathbf{J} = i\Delta T\mathbf{k}, \quad (14)$$

where the tensor T is given by the formula

$$i\Delta T = \int \mathbf{j}\mathbf{r} d\mathbf{r}, \quad (15)$$

where the product of the vectors $\mathbf{j}$ and $\mathbf{r}$ is dyadic.

In the case of electric quadrupole transitions T must be a symmetric tensor. We restrict ourselves to the case in which T in a suitable system of co-ordinates reduces to the form

$$T = \tau \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (16)$$

where τ is the electric quadrupole moment of the transition with $137^2 r_0^2$ as unit. On the other hand for magnetic dipole transitions the tensor T is antisymmetric; we consider the case

$$T = \mu \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (17)$$

where μ is the magnetic dipole moment of the transition with $137^2 r_0^2/c$ as unit.

It should be observed that the choice of the tensor T cannot be made arbitrarily but must be such as not to be in contradiction to the conditions

$$\int \rho d\mathbf{r} = 0, \quad \int \rho \mathbf{r} d\mathbf{r} = 0$$

the first of which expresses the orthogonality of the wave functions of the initial and final state of the nucleus, and the second of which expresses the impossibility of electric dipole transitions. It may be verified that the choice (16) and (17) of the tensor T fulfills these conditions.

3. DETERMINATION OF THE TENSOR S

From the definition (11) and the equations (10) and (6) we obtain immediately for the tensor S

$$S = \sum_{\sigma} \sum_{\sigma'} (u^* \mathbf{k} - \Delta \alpha u') (u' \mathbf{k} - \Delta \alpha u), \quad (18)$$

where the products of the vector-quantities are dyadic and the summations have to be carried out over all states of the electron with positive energy. We get rid of this troublesome restriction to positive energies by writing

$$u' = \frac{1}{2\epsilon'} K' u', \quad u = \frac{1}{2\epsilon} K u, \quad (19)$$

where the operators K and K' are defined by

$$K = (\alpha \cdot \mathbf{p}) + \beta + \epsilon, \quad K' = (\alpha \cdot \mathbf{p}') + \beta + \epsilon' \quad (20)$$

and give 0 when applied to the amplitudes of states with negative energy. The summations can then be carried out over all states, positive and negative, of the electron, and use can be made of the orthogonality relation

$$\sum_{\sigma} u_{\alpha}(\sigma) u_{\beta}^{*}(\sigma) = \delta_{\alpha\beta}$$

in which α and β are the spinor indices. Carrying out this summation we obtain

$$\epsilon\epsilon' S = \frac{1}{4} \text{sp}(\mathbf{k} - \Delta\alpha) K'(\mathbf{k} - \Delta\alpha) K = A - B + C, \quad (21)$$

where sp denotes the spur with respect to the spin indices and A , B and C are defined by the relations

$$\left. \begin{aligned} A &= \frac{1}{4} \text{sp}(\mathbf{k} K' \mathbf{k} K), \\ B &= \frac{1}{4} \Delta \text{sp}(\mathbf{k} K' \alpha K + \alpha K' \mathbf{k} K), \\ C &= \frac{1}{4} \Delta^2 \text{sp}(\alpha K' \alpha K). \end{aligned} \right\} \quad (22)$$

Making use of the relations

$$\alpha(\alpha \cdot \mathbf{p}) + (\alpha \cdot \mathbf{p})\alpha = 2\mathbf{p}, \quad \text{sp} \alpha_i = \text{sp} \beta = 0$$

we finally obtain

$$\left. \begin{aligned} A &= \mathbf{k} \mathbf{k} [\epsilon\epsilon' + (\mathbf{p} \cdot \mathbf{p}') + 1], \\ B &= \Delta \{ \epsilon'(\mathbf{k} \mathbf{p} + \mathbf{p} \mathbf{k}) + \epsilon(\mathbf{k} \mathbf{p}' + \mathbf{p}' \mathbf{k}) \}, \\ C &= \Delta^2 [I \{ \epsilon\epsilon' - (\mathbf{p} \cdot \mathbf{p}') - 1 \} + \mathbf{p} \mathbf{p}' + \mathbf{p}' \mathbf{p}], \end{aligned} \right\} \quad (23)$$

so that the tensor S is determined.

4. ELECTRIC DIPOLE TRANSITIONS

Since the expression (13) is independent of $\mathbf{k}$ the summation over the directions of $\mathbf{j}$ becomes identical with the summation over the directions of $\mathbf{J}$, so that by equation (12)

$$\sum_{\sigma} \sum_{\sigma'} \overline{|P|^2} = \frac{1}{3\Delta^2} (S) |\mathbf{J}|^2 = (S) |\bar{x}|^2, \quad (24)$$

where

$$\bar{x} = \int \rho x dr$$

is the geometrical dipole moment with $137r_0$ as unit, and (S) denotes the spur of S , that is, $(S) = \sum_j S_{jj}$. In the derivation of equation (24) we make use of the theorem

$$\overline{\mathbf{e}\mathbf{e}} = \frac{1}{3} I,$$

where the bar denotes that we take the average over all directions of the arbitrary unit vector $\mathbf{e}$, and I denotes the unit tensor.

It follows from equation (24) that for the dipole case we have to calculate (S). This quantity is obtained from the expression for S by writing scalar products instead of dyadic products and using the fact that (I) = 3. This gives

$$\left. \begin{aligned} (A) &= k^2\{\epsilon\epsilon' + (\mathbf{p} \cdot \mathbf{p}') + 1\}, \\ (B) &= 2\Delta\{\epsilon'(\mathbf{k} \cdot \mathbf{p}) + \epsilon(\mathbf{k} \cdot \mathbf{p}')\}, \\ (C) &= \Delta^2\{3[\epsilon\epsilon' - (\mathbf{p} \cdot \mathbf{p}') - 1] + 2(\mathbf{p} \cdot \mathbf{p}')\}. \end{aligned} \right\} \quad (25)$$

The occurrence of $(k^2 - \Delta^2)^2$ in the denominator of the expression on the right-hand side of equation (4) makes an expansion of $A - B + C$ in powers of $k^2 - \Delta^2$ desirable. This may readily be accomplished by replacing the scalar product $(\mathbf{p} \cdot \mathbf{p}')$ by $\frac{1}{2}(p^2 + p'^2 - k^2)$. An elementary calculation then gives

$$(A) - (B) + (C) = -\frac{1}{2}(k^2 - \Delta^2)^2 + (\epsilon^2 + \epsilon'^2)(k^2 - \Delta^2) - 2\Delta^2. \quad (26)$$

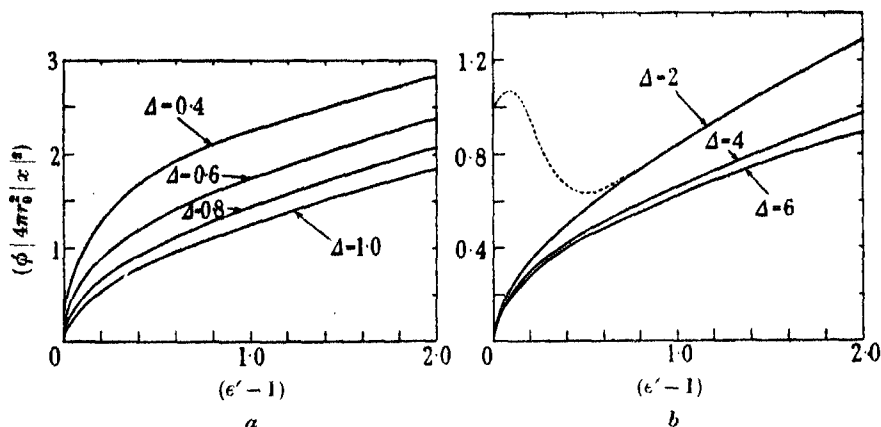


FIGURE 1. The variation of the cross-section for electric dipole transitions with excitation energy Δ and the kinetic energy of the scattered electron. The dotted curve in figure 1b corresponds to the multiplication of the cross-section by a Gamow factor as indicated in the introduction.

This expression does not contain the azimuthal angle so that the element of angular integration $d\omega$ becomes simply $2\pi d(\cos \theta)$. Now

$$d(\cos \theta) = -\frac{1}{2pp'} d(k^2)$$

and k^2 varies from $(p - p')^2$ to $(p + p')^2$, so that the integration over ω is straightforward and gives

$$\phi = 4\pi r_0^2 |x|^2 \frac{p'}{p} \left[\frac{\epsilon^2 + \epsilon'^2}{pp'} \log_e \left(\frac{\epsilon\epsilon' + pp' - 1}{\Delta} \right) - 2 \right] \quad (27)$$

after some simple modifications based on the energy-momentum relation.

In the limiting case $p \rightarrow 0$ we have $\epsilon = 1 + \Delta$ and $\epsilon' = 1$, so that equation (27) reduces to

$$\phi = 4\pi r_0^2 |x|^2 \frac{p'}{p} \left[\frac{2}{\Delta} + \Delta \right] \quad (28)$$

near the threshold of the reaction. On the other hand in the limiting case $p \rightarrow \infty$, $p' = p$, we have

$$\phi = 8\pi r_0^2 |x|^2 \left[\log_e \frac{2\epsilon^2}{\Delta} - 1 \right]. \quad (29)$$

The close resemblance of equation (29) to Bohr's formula (Bohr 1915) for the ionization losses of a charged particle should be observed.

The function $\phi/8\pi r_0^2 |x|^2$ was calculated for various values of the energy of the scattered electron and of the excitation energy Δ by means of equation (29). The results of these calculations are illustrated in figure 2.

5. ELECTRIC QUADRUPOLE AND MAGNETIC DIPOLE TRANSITIONS

If we insert from equation (14) into equation (12) we obtain in both the electric quadrupole and the magnetic dipole cases

$$\sum_{\sigma'} |P|^2 = (\mathbf{k} T S T \mathbf{k}). \quad (30)$$

If we assume that the tensor T is symmetric then the equation of continuity multiplied by $\mathbf{r}\mathbf{r}$ and integrated gives

$$\int (\nabla \mathbf{j}) \mathbf{r} \mathbf{r} d\mathbf{r} = -i\Delta \int \rho \mathbf{r} \mathbf{r} d\mathbf{r}$$

and by the symmetry property

$$\int (\nabla \mathbf{j}) \mathbf{r} \mathbf{r} d\mathbf{r} = - \int \mathbf{j} \mathbf{r} d\mathbf{r} = -i\Delta T,$$

so that the symmetrical part of the tensor T represents the geometrical quadrupole moment. Consider the symmetric tensor

$$T = \tau \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

which is the simplest case of an electric quadrupole moment of magnitude τ measured with $137^2 r_0^2$ as unit. We may write T as the difference of two dyadic products in the form

$$T = \mathbf{a}\mathbf{a} - \mathbf{b}\mathbf{b},$$

where, in the co-ordinate system we have selected,

$$\mathbf{a} = \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right), \quad \mathbf{b} = \left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0 \right),$$

so that $(\mathbf{a} \cdot \mathbf{b}) = 0$. Thus for $T\mathbf{k}$ we obtain immediately

$$T\mathbf{k} = \mathbf{a}(\mathbf{a} \cdot \mathbf{k}) - \mathbf{b}(\mathbf{b} \cdot \mathbf{k}) = \mathbf{k} \times \mathbf{c},$$

where $\mathbf{c} = \mathbf{a} \times \mathbf{b}$ is a unit vector. Inserting this expression into equation (30) we obtain therefore

$$\frac{1}{\tau^2} \sum_{\sigma} \sum_{\sigma'} |P|^2 = ((\mathbf{c} \times \mathbf{k}) S(\mathbf{c} \times \mathbf{k})).$$

To obtain the average of this expression over the initial orientations of the nucleus we calculate $\mathbf{c} \times \mathbf{k}$ by putting

$$\mathbf{k} = (k, 0, 0).$$

Hence

$$\mathbf{c} \times \mathbf{k} = (0, c_x, -c_y),$$

so that

$$\frac{1}{\tau^2} \sum_{\sigma} \sum_{\sigma'} |P|^2 = k^2 (S_{yy} c_x^2 + S_{zz} c_y^2 - 2S_{zy} c_x c_y)$$

and therefore

$$\frac{3}{\tau^2} \sum_{\sigma} \sum_{\sigma'} |\overline{P}|^2 = k^2 (S_{yy} + S_{zz}) = k^2 (S) - (\mathbf{k} S \mathbf{k}). \quad (31)$$

The quantity (S) has been calculated above—equation (26). The calculation of $(\mathbf{k} S \mathbf{k})$ proceeds along similar lines. From equations (23) we have

$$\left. \begin{aligned} (\mathbf{k} A \mathbf{k}) &= k^4 \{ \epsilon \epsilon' + (\mathbf{p} \cdot \mathbf{p}') + 1 \}, \\ (\mathbf{k} B \mathbf{k}) &= 2\Delta k^2 \{ \epsilon' (\mathbf{k} \cdot \mathbf{p}) + \epsilon (\mathbf{k} \cdot \mathbf{p}') \}, \\ (\mathbf{k} C \mathbf{k}) &= \Delta^2 \{ k^2 [\epsilon \epsilon' - (\mathbf{p} \cdot \mathbf{p}') - 1] + 2(\mathbf{p} \cdot \mathbf{k})(\mathbf{p}' \cdot \mathbf{k}) \}. \end{aligned} \right\} \quad (32)$$

and therefore after carrying out the reductions similar to those in the dipole case we have

$$(\mathbf{k} S \mathbf{k}) = \frac{1}{2\epsilon \epsilon'} \{ 4\epsilon \epsilon' (k^2 - \Delta^2)^2 - (k^2 - \Delta^2)^3 \}. \quad (33)$$

Substituting from equations (26) and (33) into equation (31) we have

$$\sum_{\sigma} \sum_{\sigma'} |\overline{P}|^2 = \frac{\tau^2 \Delta^2}{6\epsilon \epsilon'} \{ (k^2 - \Delta^2)^2 + 2(p^2 + p'^2)(k^2 - \Delta^2) - 4\Delta^2 \}. \quad (34)$$

Inserting from this equation into equation (4) and integrating over the directions of the scattered electron we obtain finally for the cross-section in the case of electric quadrupole transitions

$$\phi = \frac{4\pi}{3} \tau_0^2 \tau^2 F(\epsilon', \Delta), \quad (35)$$

where the function $F(\epsilon', \Delta)$ is defined by the equation

$$F(\epsilon', \Delta) = \frac{p^2 + p'^2}{p^2} \log_e \left(\frac{\epsilon \epsilon' + p p' - 1}{\Delta} \right) \Delta^2. \quad (36)$$

It follows immediately from equations (35) and (36) that as $p' \rightarrow 0$

$$\phi \rightarrow \frac{4\pi}{3} \tau_0^2 \tau^2 \Delta (2\Delta + \Delta^2)^{\frac{1}{2}} p'$$

and that as $p, p' \rightarrow \infty$,

$$\phi \rightarrow \frac{8\pi}{3} \tau_0^2 \tau^2 \Delta^2 \log_e \left(\frac{2p^2}{\Delta} \right).$$

Values of the function $F(\epsilon', \Delta)$ were calculated for various values of the energy ϵ' and of the excitation energy Δ , by means of equation (36). The variation of this function with ϵ' and Δ is shown graphically in figure 2.

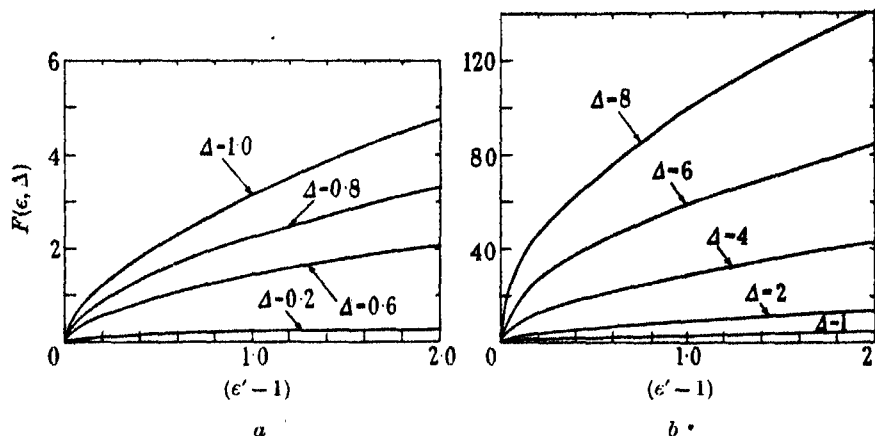


FIGURE 2. The variation of the function $F(\epsilon', \Delta)$ with ϵ' and Δ . The cross-section in the electric quadrupole case is obtained by multiplying F by $4\pi r_0^2 \tau^2/3$; the corresponding factor in the magnetic dipole case is $4\pi r_0^2 \mu^2/3$.

In the case of magnetic dipole transitions the tensor T occurring in equation (30) may be taken to have the form (17). Introducing unit vectors $\mathbf{e}_x, \mathbf{e}_y$ orthogonal to one another we may write

$$T = \mu(\mathbf{e}_x \mathbf{e}_y - \mathbf{e}_y \mathbf{e}_x) \quad (37)$$

from which it follows immediately that

$$T\mathbf{k} = \mu(\mathbf{e}_x k_y - \mathbf{e}_y k_x).$$

From the definition (11) of the tensor S we then have

$$\sum_{\sigma} \sum_{\sigma'} |P|^2 = \mu^2 \sum_{\sigma} \sum_{\sigma'} |(s_x k_y - s_y k_x)|^2 = \mu^2 \sum_{\sigma} \sum_{\sigma'} |\mathbf{s} \times \mathbf{k}|_z^2$$

and averaging over the initial orientations in space of the nucleus we obtain

$$\sum_{\sigma} \sum_{\sigma'} \overline{|P|^2} = -\frac{1}{3} \mu^2 (\mathbf{k} \times \mathbf{S} \times \mathbf{k}). \quad (38)$$

It follows from equation (23) that since both A and B contain the vector $\mathbf{k}$ in the dyadic products that

$$(\mathbf{k} \times A \times \mathbf{k}) = (\mathbf{k} \times B \times \mathbf{k}) = 0,$$

so that only the term C gives a non-vanishing contribution. Furthermore

$$(\mathbf{k} \times I \times \mathbf{k}) = -2k^2,$$

so that with the definition (23) we have after a little reduction

$$\sum_{\sigma} \sum_{\sigma'} \overline{|P|^2} = \frac{\mu^2 \Delta^2}{6\epsilon\epsilon'} \{ (k^2 - \Delta^2)^2 + 2(p^2 + p'^2)(k^2 - \Delta^2) - 4\Delta^2 \}. \quad (39)$$

Comparing this formula with equation (34) we see that the integrations over the directions of the scattered electrons are the same as in the electric quadrupole case leading to

$$\phi = \frac{4\pi}{3} r_0^2 \mu^2 F(\epsilon', \Delta), \quad (40)$$

where $F(\epsilon', \Delta)$ is defined by equation (36).

6. DISCUSSION

It will be observed from figures 1 and 2 that in all three types of transitions considered here the cross-section increases with increasing kinetic energy of the scattered electron. Near the threshold energy the form of all the curves is parabolic, but for large values of the kinetic energy it is logarithmic. The difference between the curves for electric dipole transitions and those for higher order transitions arises from the difference of their dependence on the threshold energy. In the former case the cross-section decreases as the threshold energy Δ increases (the kinetic energy of the scattered electron being kept constant).

In the equations (28) and (35) the quantities $|x|^2$ and τ^2 still remain to be calculated. This can be most conveniently done by the use of the liquid-drop model (Bohr & Kalckar 1936; Bethe 1937). In this model of the nucleus the electric and magnetic dipole-moments vanish and only quadrupole and higher order radiation can occur. The vanishing of the electric dipole moment arises from the fact, that in this model, the centre of gravity of the protons coincides with the centre of gravity of the nucleus as a whole. That there is no magnetic dipole moment is due to the lack of rotational components in the displacement current. A model which might give a magnetic dipole moment is the rigid rotator model recently proposed by Guggenheimer (1942).

In the liquid-drop model the frequency of the l th harmonic of the surface wave is given by the formula

$$\omega^2 = \frac{G}{\rho S R^3} (l+2)l(l-1),$$

where G is the surface energy, $9.6A^{\frac{1}{2}}$ MeV, ρ is the density and S the surface of the nucleus. The mode $l = 2$ is the only one giving a contribution to the electric quadrupole moment. The energy of the first excited level is ω so that taking the nuclear radius to be $1.6 \times 10^{-13} A^{\frac{1}{2}}$ cm. we obtain

$$\Delta = 38.7 A^{-\frac{1}{2}} \quad (41)$$

giving first excitation levels at 4.95 MeV for oxygen and 1.27 MeV for uranium. In the liquid-drop model the quadrupole moment of the nucleus is given by the equation

$$\tau = \frac{Z R_0 b A^{\frac{1}{2}}}{5 \lambda_0^2}, \quad (42)$$

where b , the amplitude of the second harmonic is related to Δ by

$$mc^2 \Delta = 2Gb^2/15R^2. \quad (43)$$

Combining equations (41), (42) and (43) we obtain

$$\tau = 1.22 Z A^{\frac{1}{2}} \cdot 10^{-6} \quad (44)$$

for the quadrupole moment corresponding to the transition from the ground state to the first excited state. Substituting from equation (44) into equation (35) we may calculate the cross-section for this process.

For cadmium ($Z = 48$) we may compare the value 1.9 MeV for $mc^2\Delta$ given by equation (41) with the experimentally observed value 1.3 MeV. This gives us some measure of the validity of the use of the liquid-drop model and the accuracy to be expected from the calculations of the cross-sections based upon the use of this model. For cadmium equation (44) gives $\tau = 0.85 \times 10^{-3}$ and for a kinetic energy of the scattered electron equal to 100 kV and $\Delta = 3.8$ it follows from linear interpolation of the curves of figure 2, that $F(\epsilon', \Delta)$ is approximately equal to 10. As a consequence of equation (35) we find that the corresponding cross-section is of the order $2 \times 10^{-30} \text{ cm}^2$.

This is in excess of the value 10^{-32} cm^2 estimated by Collins & Waldmann (1940) for indium but not violently so when we consider the limitations inherent in the use of the liquid-drop model and the assumptions which Collins & Waldmann had to introduce about the efficiency of their counters in deriving the experimental estimate of the cross-section. On the other hand if we use Collins's estimate of the cross-section to calculate the quadrupole moment of the transition with the help of equation (35) we find that it comes out to be of the order 10^{-25} cm^2 which is small but within the possible range for this quantity. Moreover there is no reason to believe that the process observed does not correspond to a higher order transition than the electric quadrupole. Indeed the cross-section for electric octupole transitions should be smaller by a factor of order $(137r_0/R)^2$ (r_0 = Lorentz-radius of the electron, R = radius of the nucleus) which in the case of indium is about 1600 leading to a cross-section in fair agreement with the estimate of Collins & Waldmann.

The other possible experimental test of the theory on the other hand—the experiments on electron-excitation of cadmium by Wiedenbeck (1945)—unfortunately concerns the region in which Born's approximation breaks down. The general trend, however, of Wiedenbeck's excitation curves may be well understood by means of the above considerations though a direct comparison would require a more detailed theory of the behaviour of the excitation curves near the threshold.

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The mechanism of the carbon dioxide-carbon reaction

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The detailed mechanism of the reaction between carbon dioxide and coconut shell charcoal has been studied by both flow and static methods. The temperature has been varied in the range 700 to 830° C and the pressures of the gases from 10 to 760 mm.

The static method has been used to investigate the adsorption of the gases on the carbon surface during the course of the reaction, and thus to illustrate in a very direct way the general nature of the mechanism. Accurate measurements of the rate of reaction have been made by the flow method. At a given temperature the rate of reaction can be represented in terms of the partial pressures of the gases by an expression of the form

$$\text{rate} = \frac{k_1 p_{\text{CO}_2}}{1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}}$$

The three separate constants have been evaluated and each has been found to vary exponentially with temperature. From these results the rates of the individual stages of the mechanism have been calculated.

The first stage is the decomposition of the carbon dioxide molecule into an atom of oxygen which is adsorbed by the carbon and a molecule of carbon monoxide which passes into the gas phase. Only certain sites on the charcoal surface take part in the reaction; they represent about 0.5 % of the total area and probably consist of some of the less firmly bound carbon atoms situated at lattice discontinuities. The rate of the first stage can be accounted for by assuming that reaction occurs in those collisions in which the combined energy of the active carbon atom and the incident carbon dioxide molecule exceeds 68 kcal. The second stage is the evaporation of the adsorbed oxygen atom, together with an atom of carbon from the solid, to form gaseous carbon monoxide; the activation energy is thought to be 38 kcal., and the low value of 10^7 sec.^{-1} obtained for the non-exponential factor is discussed.

The retarding effect of carbon monoxide is due to the adsorption of the gas on the reaction sites, the heat given out in the change being 46 kcal. On the basis of this value, which implies that the molecule is adsorbed chemically, it is possible to calculate theoretically the order of magnitude of the retardation constant, k_3 .

INTRODUCTION

This investigation forms part of a comprehensive study of the reactions of the steam-carbon system. The effect on the separate reactions of changes in the partial pressures of the gases has been described in a previous paper (Gadsby, Hinshelwood & Sykes 1946), in which the general interpretation of the main kinetic relationships was also discussed. In continuation of this work, the detailed mechanism of the reactions in which solid carbon is converted into gaseous carbon monoxide has now been studied. The present paper deals with the results obtained for the carbon dioxide-carbon reaction, and an accompanying one with those for the steam-carbon reaction.

OUTLINE OF METHOD

The principle of the method is the complementary use of both the flow and the static techniques. The variation of the rate of reaction with the partial pressures of

the gases and with temperature is determined with a flow apparatus. This technique is the most accurate one for the purpose, since a steady state under any desired conditions can be maintained while the measurement is being made. The results, however, refer to a whole sequence of elementary processes and can be interpreted, as shown previously, in terms of a number of different kinetic schemes. In order to decide between the various possibilities, the adsorption of the gases during the course of the reaction is studied with a static apparatus. These experiments provide the information which is required to calculate the rates of the individual stages from the results obtained by the flow method.

Both the carbon dioxide reaction and the steam reaction are investigated with samples of the same coconut shell charcoal. Although this material contains a small percentage of catalytic impurities, its behaviour has been shown to be similar to that of many different types of carbon (Gadsby *et al.* 1946). It is probable, therefore, that the impurities merely influence the rate of one or more stages of a kinetic scheme characteristic of carbon in general. The properties of the impure substances are of considerable practical importance, and their study is also an essential step in the solution of the problem presented by the catalysis.

EXPERIMENTAL TECHNIQUE

The flow apparatus is similar to that described previously (Gadsby *et al.* 1946), but greater accuracy is obtained by the use of an improved method of temperature control (Gadsby & Sykes 1948), which regulates automatically the distribution of temperature in space as well as in time. In this way the temperature is kept uniform to within 2°C over the whole charcoal column and does not vary by more than $\pm 0.5^{\circ}\text{C}$ at any point. During each run the controlling thermocouple is standardized against a platinum/platinum-rhodium one. Improvement has also been made in the calibration of the flowmeters, for which an accuracy of $\pm 0.3\%$ is obtained. The amount of charcoal is varied from 35 g. at the lowest temperature to 8 g. at the highest temperature. This ensures that only a small fraction of the carbon dioxide reacts, and consequently that its partial pressure and the total rate of flow are approximately uniform throughout the reaction zone. To allow for the change during each experiment in the amount of charcoal present, the rate of reaction for a given composition of the gas stream is measured at least twice, and the results are adjusted by interpolation to refer to 85 % of the initial amount of charcoal. In all other respects the technique of the measurements is the same as in the previous investigation.

In the static apparatus the charcoal is contained in a silica vessel heated in an electric furnace. Unless otherwise stated, the volume of the vessel is 290 c.c. and the amount of charcoal 10 g. The temperature is measured with a platinum/platinum-rhodium thermocouple, and is controlled to within $\pm 0.5^{\circ}\text{C}$ by means of a platinum resistance thermometer in conjunction with a relay circuit of the type described by Coates (1944). Gases to be introduced are first admitted to a section of the

apparatus of known volume fitted with a mercury manometer; the amount subsequently transferred to the reaction vessel can then be calculated from the external decrease in pressure. Another mercury manometer measures the pressure in the reaction vessel, and the composition is determined by withdrawing samples which are analyzed with a Haldane or with a Bone & Wheeler apparatus. To study the course of the reaction, a series of experiments is made in which the same amount of gas is allowed to remain in contact with the charcoal for a series of different times. Between each experiment the reaction vessel is evacuated at the working temperature by a mercury vapour pump for a time sufficient to ensure reproducibility. For this purpose periods of from 10 min. to a few hours were found to be adequate.

RESULTS

(1) The flow method

The general form of the results

Measurements are made at six temperatures in the range 734 to 829° C. The variation of the rate of reaction with the partial pressure of carbon dioxide is determined by passing through the charcoal column a series of carbon dioxide-nitrogen mixtures, the rate of flow of nitrogen being chosen so as to keep the total rate of flow constant at 1200 c.c./min. The rate of reaction, defined as one-half the rate of formation of carbon monoxide per g. of charcoal, is plotted against the initial partial pressure of carbon dioxide on the left-hand side of figure 1. At each temperature the reaction is of fractional apparent order. To determine the effect of carbon monoxide, various small partial pressures of it are added, the partial pressure of carbon dioxide and the total rate of flow being kept constant by adjustment of the rate of flow of nitrogen. The conditions are such that the rate of the reverse reaction is negligible. The right-hand side of figure 1, where the rate of reaction is plotted against the initial partial pressure of carbon monoxide, shows that there is a strong retardation over the whole temperature range. It may be noted that the percentage reduction in the rate for a given increase in the partial pressure of carbon monoxide is more marked the lower the temperature.

The rate expression

It will first be established that the results at any given temperature can be represented by an expression of the form

$$\text{rate} = \frac{k_1 p_{\text{CO}_2}}{1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}} \quad (1)$$

It follows from the treatment outlined previously (Gadsby *et al.* 1946) that under certain conditions equation (1) leads to the relation

$$\frac{m}{x} = \frac{1 + k_3 p_{\text{CO}_2}^0}{k} + \frac{k_2 \bar{p}_{\text{CO}}}{k} \quad (2)$$

In the above, x is the fraction of the carbon dioxide reacting, m is the mass of the charcoal, the superscript zero denotes the initial value and $\bar{p}_{\text{CO}}$ is the average partial pressure of carbon monoxide; k is now defined by the equation

$$k = k_1 RT/V, \quad (3)$$

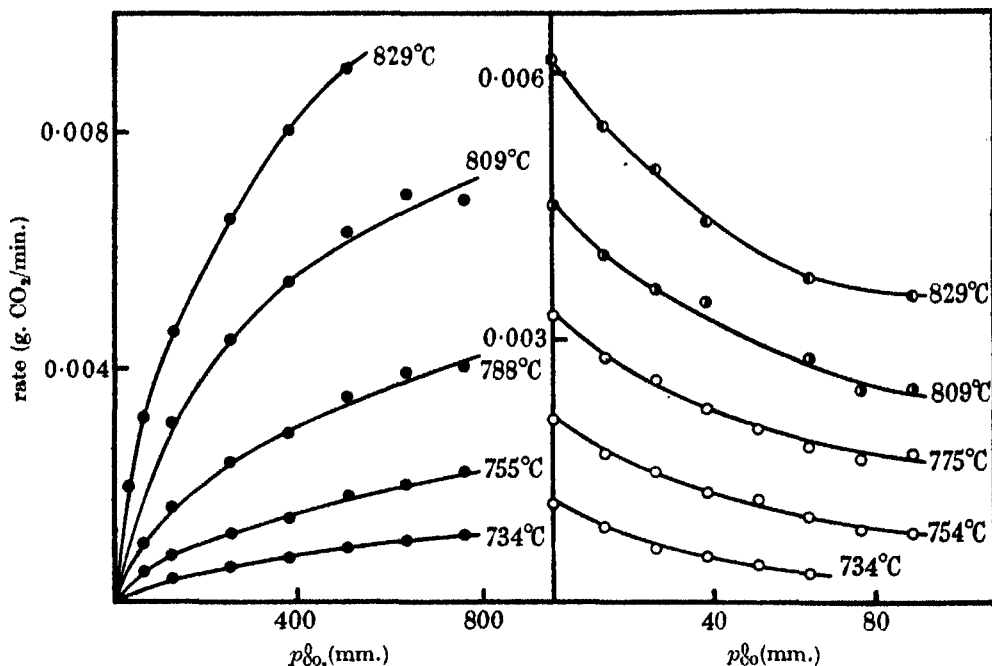


FIGURE 1. Apparent order of reaction with respect to carbon dioxide and retardation by carbon monoxide. Initial pressure of CO_2 : $\circ$ 633 mm.; $\bullet$ 253 mm.; $\bullet$ 127 mm.

where V is the total rate of flow at the temperature T of the reaction zone. The conditions which must be satisfied for equation (2) to be applicable are as follows:

- (i) the total rate of flow is constant throughout the reaction zone;
- (ii) the rate of diffusion in the direction of flow is negligible compared with the rate of flow;
- (iii) $\ln(1-x)$ may be expanded with neglect of powers of x greater than the second;
- (iv) $2k_2 p_{\text{CO}_2}^0 \gg 1$ and $2p_{\text{CO}_2}^0 > p_{\text{CO}}^0$.

These requirements are fulfilled to a close approximation. The total rate of flow does not vary by more than 3.8 %, and the rates of diffusion can be shown by rough calculation to be less than 2.5 % of the rates of flow. The fraction of carbon dioxide reacting rarely exceeds 0.10 and is never greater than 0.17. The average value of $2k_2 p_{\text{CO}_2}^0$ is of the order of 50 and $2p_{\text{CO}_2}^0/p_{\text{CO}}^0$ is not less than 2.8.

Equation (2) may therefore be used to test the rate expression by plotting m/x against $\bar{p}_{\text{CO}}$ for various values of $p_{\text{CO}_2}^0$. The typical results shown in figure 2 are

well represented by straight lines as required by equation (2). The slope at a given temperature should be equal to k_2/k and should thus be independent of $p_{\text{CO}_2}^0$; the slight variation observed is not systematic and is probably due to lack of complete reproducibility from one experiment to another. In figure 3 the intercept m/x_0 at

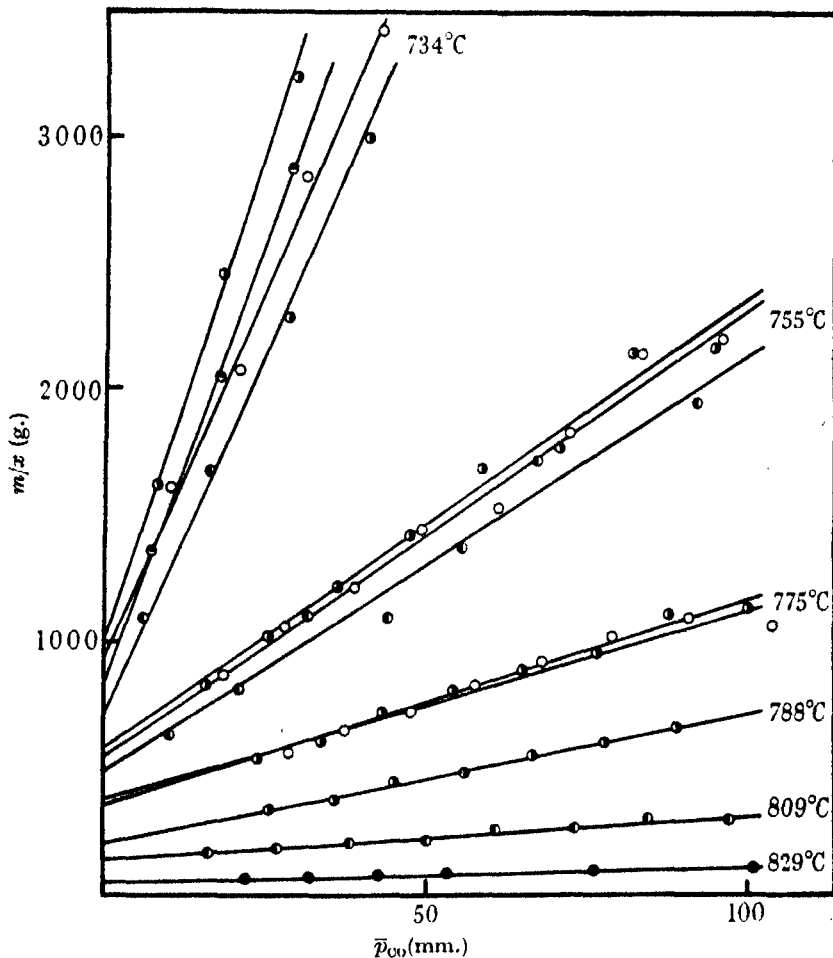


FIGURE 2. Test of rate expression: variation of carbon monoxide pressure. Initial pressure of CO_2 : $\circ$ 633 mm.; $\bullet$ 506 mm.; $\bullet$ 380 mm.; $\bullet$ 253 mm. and $\bullet$ 127 mm.

$\bar{p}_{\text{CO}} = 0$ is plotted against $p_{\text{CO}_2}^0$. These intercepts are calculated by subtracting $k_2 \bar{p}_{\text{CO}}/k$ from the values of m/x obtained in the experiments where the carbon dioxide pressure is varied without the addition of carbon monoxide. It can be seen that the linear relation

$$\frac{m}{x_0} = \frac{1 + k_2 p_{\text{CO}_2}^0}{k} \quad (4)$$

required by equation (2) is obeyed within the limits of error at each temperature.

The rate of reaction can thus be represented closely by equation (1). The values of k_1 and k_3 are calculated from the slopes and intercepts of figure 3, and those of k_2 from the slopes of figure 2; all straight lines are drawn by the method of least squares, and the probable errors of the constants are estimated from the residuals in the usual way. In figure 4 the logarithms of k_1 , k_2 and k_3 are plotted against the

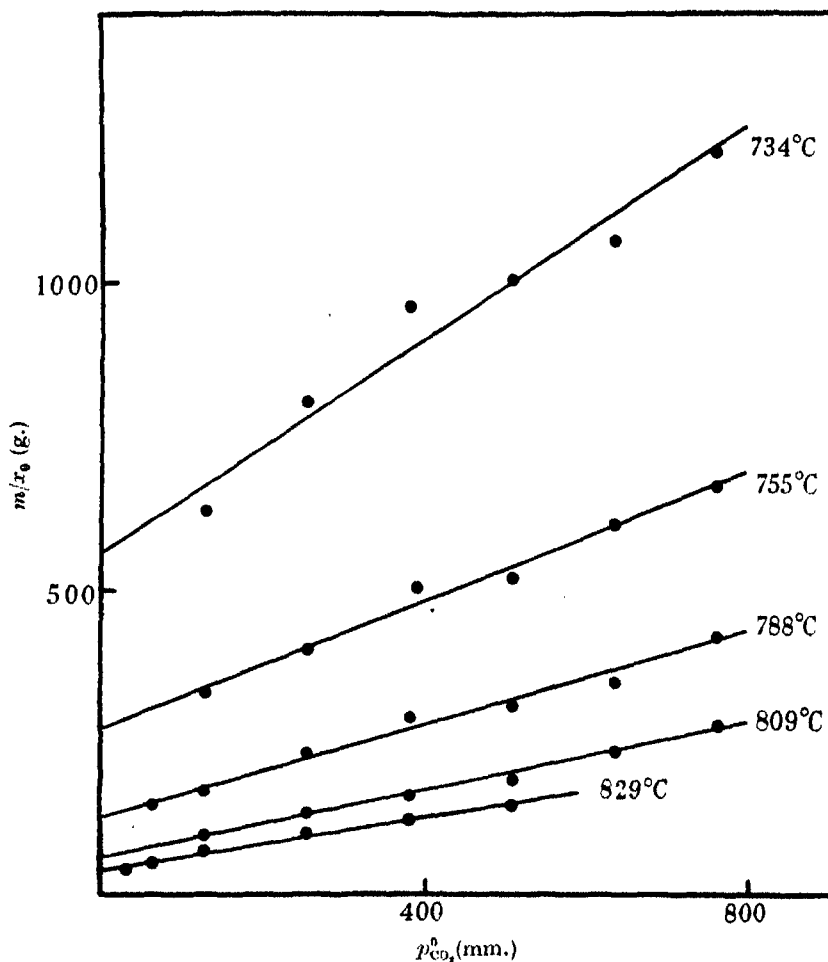


FIGURE 3. Test of rate expression: variation of carbon dioxide pressure.

reciprocal of the absolute temperature, the radii of the circles being equal to the probable errors. The variation of all three constants with temperature is adequately represented by the straight lines drawn by the method of least squares. A concise summary of the measurements may thus be given as follows:

$$k_1 = k_{01} e^{-E_1/RT}, \quad \text{where} \quad k_{01} = 10^{8.8 \pm 0.6} \text{ g.mol.min.}^{-1} \text{ atm.}^{-1} \text{ g.}^{-1},$$

$$\text{and} \quad E_1 = 58.8 \pm 2.6 \text{ kcal.g.mol.}^{-1};$$

$$k_2 = k_{02} e^{+E_2/RT}, \quad \text{where } k_{02} = 10^{-7.9 \pm 0.7} \text{ atm.}^{-1},$$

$$\text{and } E_2 = 45.5 \pm 3.5 \text{ kcal.g.mol.}^{-1};$$

$$k_3 = k_{03} e^{-E_3/RT}, \quad \text{where } k_{03} = 10^{6.5 \pm 0.7} \text{ atm.}^{-1},$$

$$\text{and } E_3 = 30.1 \pm 3.6 \text{ kcal.g.mol.}^{-1}.$$

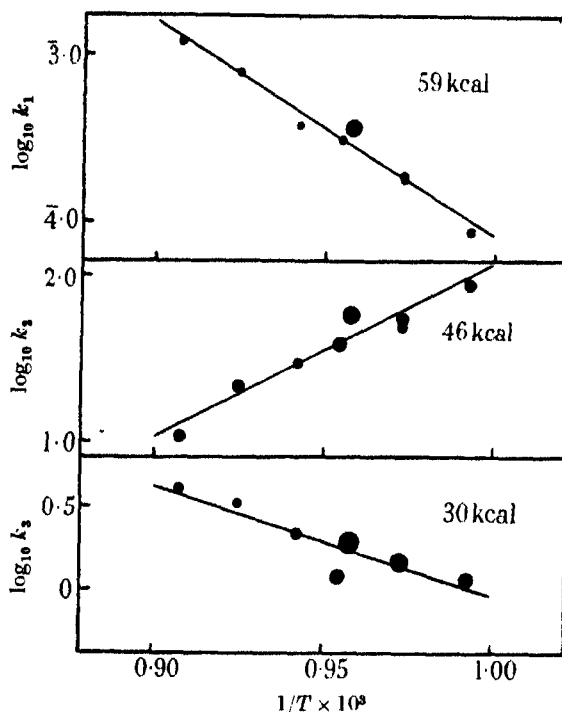


FIGURE 4. Variation of k_1 , k_2 and k_3 with temperature.

The question of diffusion

It will be shown that the above constants are independent of the total rate of flow, and thus that the reaction is not controlled by diffusion outside the charcoal granules. The experimental points in figure 5 represent the rate of reaction as a function of the total rate of flow. The curves are calculated from the rate expression assuming that k_1 , k_2 and k_3 are constant, but allowing for the change in the partial pressure of carbon monoxide. They are obtained by solving for x as a function of V in the expression

$$\frac{1}{xV} = \frac{1 + k_3 p_{\text{CO}_2}^0}{mk_1 RT} + \frac{k_2 (p_{\text{CO}}^0 + x p_{\text{CO}_2}^0)}{mk_1 RT}, \quad (5)$$

which follows from equations (2) and (3); the constant terms $(1 + k_3 p_{\text{CO}_2}^0)/mk_1 RT$ and $k_2/mk_1 RT$ are evaluated from the two rates of reaction at 1200 c.c./min. at each temperature. The agreement between the experimental points and the calculated curves shows that the observed effect is caused entirely by the change in

the partial pressure of the carbon monoxide formed, resulting from the change in the rate of flow. The much smaller variation of the lower set of experimental points at each temperature, obtained in the presence of an added partial pressure of carbon monoxide, large compared with that formed in the reaction, strongly supports the above interpretation. Thus, as previously observed with the coal charcoal, diffusion outside the granules is not an important factor. This conclusion is consistent with the exponential variation of the rate of reaction with temperature, which also rules out the possibility of serious interference by diffusion inside the granules.

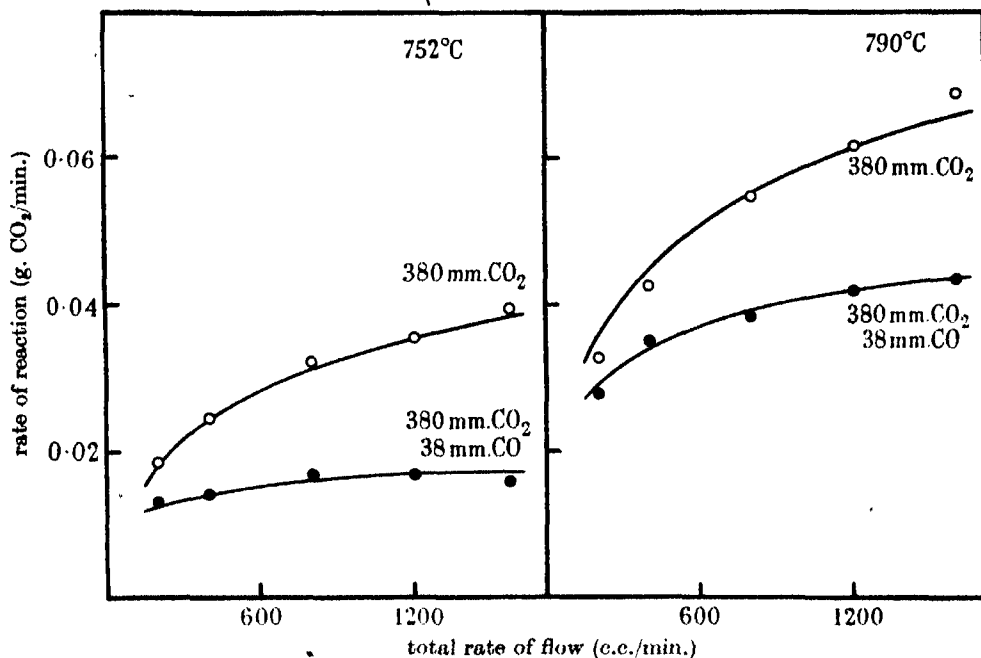


FIGURE 5. Variation of total rate of flow. Comparison of experimental points with curves calculated from equation (5).

(2) *The static method*

The course of reaction

Figure 6 shows the changes which occur both in the gas phase and on the carbon surface, when carbon dioxide is admitted to a vessel of volume 179 c.c. containing 5 g. of charcoal. The initial pressure, $p_{\text{CO}_2}^0$, is the pressure which the carbon dioxide would exert if neither adsorption nor reaction took place; it is calculated, on the basis of calibration experiments with argon, from the amount of gas introduced. The amount of oxygen adsorbed is expressed as the pressure which it would exert as carbon monoxide in the gas phase, and is taken to be $2p_{\text{CO}_2}^0 - (2p_{\text{CO}_2} + p_{\text{CO}})$. This stoichiometric definition makes no assumptions about the state of the oxygen on the surface and thus includes that present either as adsorbed carbon monoxide or in any other form.

Initially there is a rapid decrease in the pressure of carbon dioxide; it is accompanied by a slightly smaller increase in the amount of oxygen adsorbed and by a slightly larger increase in the pressure of carbon monoxide. The first stage is thus the reaction of the carbon dioxide with the surface to give an atom of oxygen which is adsorbed and a molecule of carbon monoxide which passes into the gas phase:

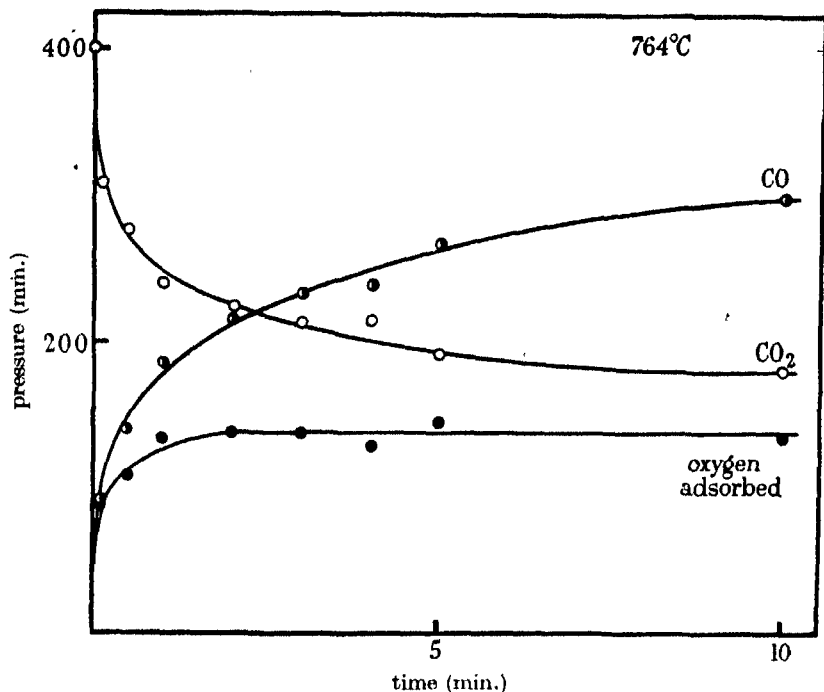


FIGURE 6. The course of reaction. A change of pressure of 1.0 mm. is equivalent in amount of reaction per g. of charcoal to a change of 0.81 mm. in figures 7, 8 and 9.

This result is in agreement with the work of Langmuir (1915) with graphite, of Broom & Travers (1932) with coconut shell charcoal and of Semechkova & Frank-Kamenetzky (1940) with sugar charcoal. The second stage is presumably the evaporation of the oxygen as carbon monoxide:



The rate of reaction might thus be expected to be proportional to the amount of oxygen absorbed, once an approximately steady value of the latter has been established. However, it can be seen from figure 6 that, although the rate of reaction falls continually, the amount of oxygen adsorbed at first rises and then remains substantially constant. Further evidence for the behaviour of the oxygen is given in figure 7, where the reaction is followed much more nearly to completion. Two explana-

tions may be proposed; the progressive adsorption of carbon monoxide may compensate for the expected decrease in the amount of oxygen which is transferred from carbon dioxide to the surface, or the reaction may take place on sites of successively decreasing reactivity. That the adsorption of carbon monoxide is an important factor is suggested by the following experiments.

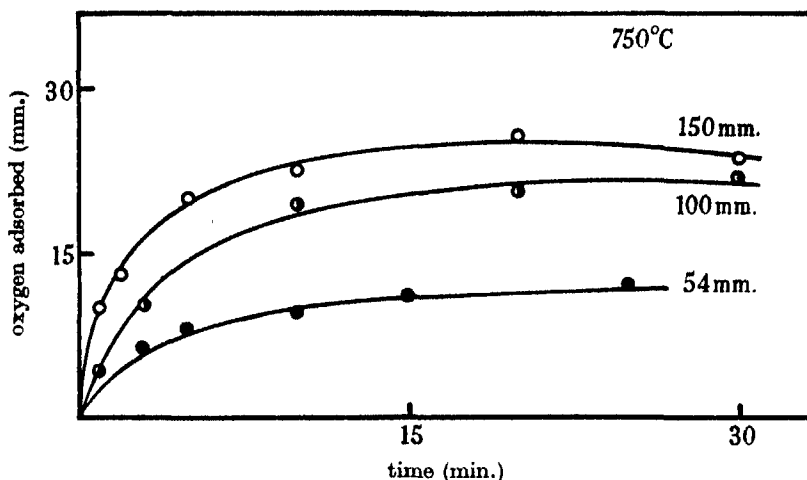


FIGURE 7. The amount of oxygen adsorbed during the reaction. Each curve is labelled with the initial pressure of carbon dioxide.

TABLE 1

p_{CO_2} (mm.)	p_{CO} (mm.)	oxygen adsorbed (mm.)
25	228	25
58	263	25
96	276	29
125	304	35
23	134	21
53	169	26

Mixtures of carbon dioxide at various pressures and of carbon monoxide at a large constant pressure are introduced, and analyses are made after each mixture has been in contact with the charcoal for 20 min. Typical results obtained at 750°C are recorded in the first four rows of table 1.

The wide variation in the pressure of carbon dioxide is not accompanied by a corresponding change in the amount of oxygen adsorbed, which follows more closely the smaller variation in the pressure of carbon monoxide. A large part of the oxygen on the surface during the later stages of the reaction is thus probably due to the adsorption of carbon monoxide. The figures in the last two rows were obtained without the addition of carbon monoxide. Comparison with the values above shows that, at constant pressure of carbon dioxide, the amount of oxygen adsorbed does

not vary greatly with change in the pressure of carbon monoxide. This result can be understood on the basis of the competitive adsorption of oxygen from carbon dioxide and of carbon monoxide. It also implies that the alternative retardation mechanism, represented by the reverse of equation (6), does not in fact make any important contribution; otherwise increase in the pressure of carbon monoxide would lead to a marked decrease in the amount of oxygen adsorbed. It is probable, therefore, that the adsorption of carbon monoxide is the factor which causes the reaction to be retarded by that gas.

The adsorption of carbon monoxide

The following results show that the behaviour of carbon monoxide is consistent with the proposed mechanism of reaction. In figure 8 the decrease of pressure which occurs when the gas is introduced is plotted against time. Since only small amounts

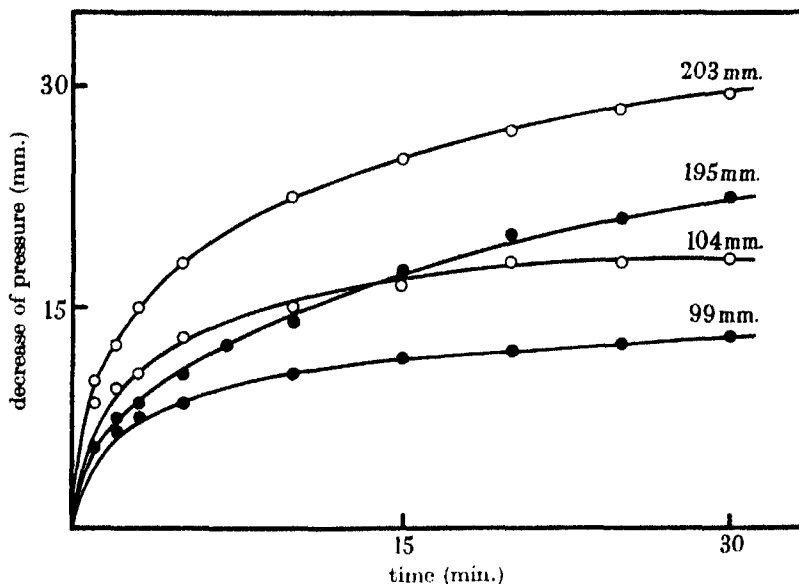


FIGURE 8. The rate of adsorption of carbon monoxide. ○ 850° C; ● 800° C.

of carbon dioxide are formed, the curves represent closely the extent to which carbon monoxide is adsorbed. Comparison with figure 6 shows that the adsorption is slow compared with the initial reaction of carbon dioxide. Within 10 min., however, the greater part of the adsorption has taken place, so that the process might be expected to be significant in the later stages of the reaction. The amount finally adsorbed, taken as the decrease of pressure less that of the carbon dioxide formed, is plotted in figure 9 against the pressure of the carbon monoxide remaining in the gas phase. It can be seen that the amount of oxygen on the surface in the later stages of the reaction (table 1) is similar to the amount of carbon monoxide which would be

adsorbed. However, while the extent to which carbon monoxide retards the reaction decreases rapidly as the temperature is raised (k_2 , figure 4), the adsorption isotherm is roughly independent of temperature. To avoid this difficulty, it may be supposed that, in addition to its reversible exothermic adsorption on the reaction sites, carbon monoxide is also adsorbed on less active parts of the surface. If equilibrium was not established with respect to these latter sites, the number occupied would increase with rise of temperature, and the total adsorption might thus remain approximately constant.

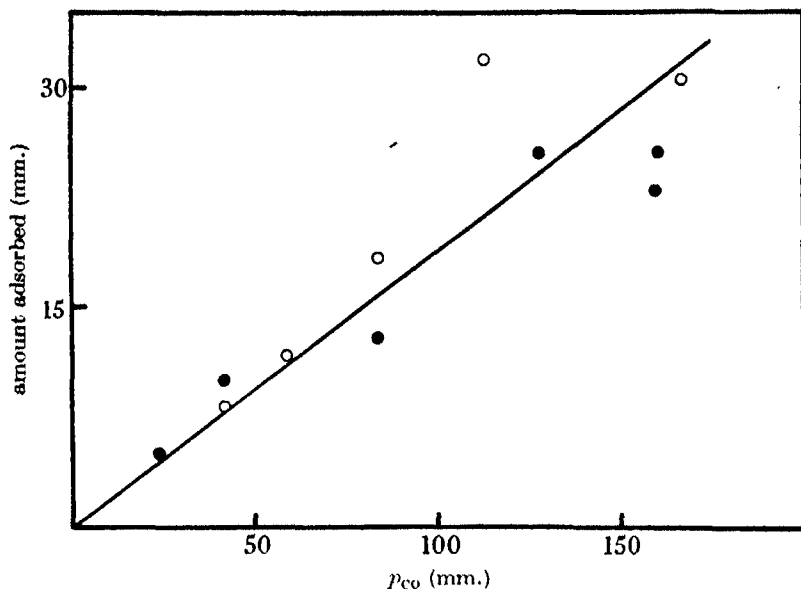


FIGURE 9. The amount of carbon monoxide adsorbed. ○ 850° C; ● 800° C.

The total area of the charcoal has been estimated from the adsorption isotherm for water vapour at room temperature to be $3 \times 10^6 \text{ cm.}^2 \text{ g.}^{-1}$ (Kipling, unpublished work). To cover this area with a close-packed layer of carbon monoxide about $3 \times 10^{-3} \text{ g.mol.}$ would be required. Up to $1.5 \times 10^{-5} \text{ g.mol.}$ of carbon monoxide is adsorbed by 1 g. of charcoal (figure 9) and the largest amount of oxygen ever observed on the surface during the reaction (figure 6) is equivalent to $8.7 \times 10^{-5} \text{ g.mol.g.}^{-1}$. It is clear, therefore, that only a small fraction of the charcoal surface takes part in the reaction under these conditions. The estimation of the area represented by the active sites is complicated by the assumption that carbon monoxide may also be adsorbed on other parts of the surface, but 0.5 % of the total area is thought to be of the correct order of magnitude.

The effect of argon and nitrogen

The assumption that diffusion is not an important factor, even in the static apparatus, can be justified by the fact that the reaction is not retarded by an inert

gas. Figure 10 shows that the addition of argon sufficient to increase the total pressure by a factor of four is without effect on the reaction. Although these experiments rule out the possibility that conditions outside the charcoal granules might have been different in the absence of the flow, they add no information to that provided by the temperature coefficient about the situation in the finer pores inside the granules. There the rate of diffusion is limited by collisions with the walls, since the diameter of the pores is of the order of 10^{-7} cm. (Kipling, unpublished work), and is thus smaller than the mean free path of about 10^{-4} cm. at a pressure of 200 mm. Analogous experiments with nitrogen, also illustrated in figure 10, show that this gas has no specific effect on the reaction, and so justify its use as the inactive carrier in the flow apparatus.

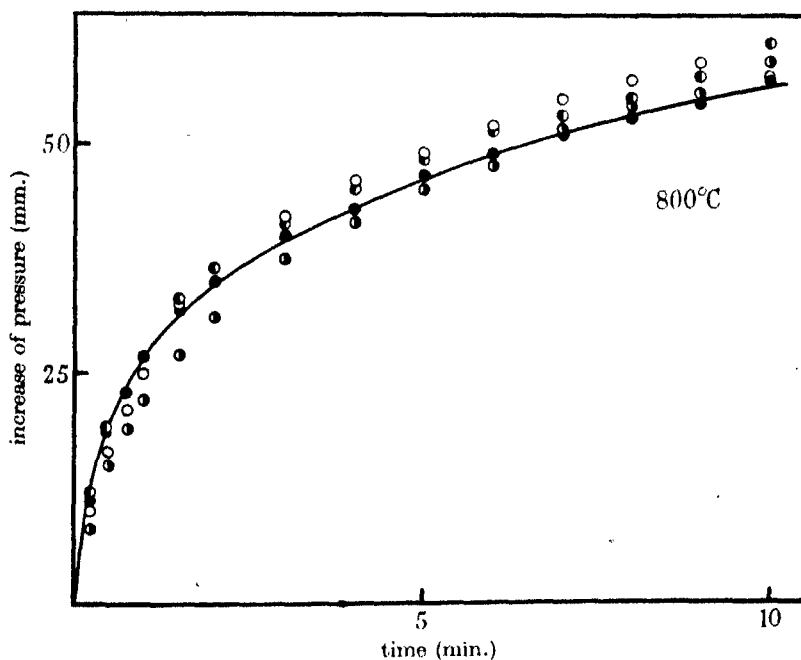


FIGURE 10. The effect of argon and nitrogen. Carbon dioxide at an initial pressure of 110 mm. in the presence of ● no added gas; ◐ 198 mm. argon; ● 299 mm. argon; ○ 294 mm. nitrogen.

The rate of reaction

Although the static method is unsuitable for accurate measurement of the rate of reaction, the following observations provide some further support for the conclusions which have already been reached.

In table 2 the rate of reaction is compared with the values expected on the basis of the flow experiments. The first two columns give the pressures of carbon dioxide and carbon monoxide at various stages of the reaction represented in figure 6. The

observed rates of reaction are obtained by drawing tangents to the graph of the total pressure as a function of time, and the calculated ones by substituting in equation (1) the pressures in the first two columns and the values of the constants obtained in the flow experiments. A small correction is also made for the reverse reaction. Although initially the observed rate exceeds the calculated one, there is good agreement in the later stages. However, since it is only adsorbed slowly, the carbon monoxide formed in the initial reaction of the carbon dioxide with the surface cannot exert its full retarding effect immediately; it is only in the later stages that a steady state should be approached. The alternative retardation mechanism, represented by the reverse of equation (6), would require the untenable hypothesis that the initial reaction of the carbon dioxide at first goes far beyond an equilibrium position to which it subsequently returns. If the initial transfer of the oxygen atom to the surface takes place in an end-on collision of the carbon dioxide molecule, there is, however, no reason why the carbon monoxide formed simultaneously should not pass directly into the gas phase and only be adsorbed subsequently. The possibility that the high initial rate of reaction is due to the greater intrinsic reactivity of the fresh carbon surface would appear to be ruled out by the following experiments.

TABLE 2

p_{CO_2} (mm.)	p_{CO} (mm.)	rate of reaction	
		observed (mm.min. ⁻¹)	calculated (mm.min. ⁻¹)
308	92	36	23
260	160	24	12
232	200	13	8.5
212	240	7	6.5
192	280	4.5	4.5
182	300	4	4

TABLE 3

temp. (° C)	$k_1 \times 10^4$ (g.mol _g min. ⁻¹ atm. ⁻¹ g. ⁻¹)	
	static	flow
690	0.10	0.26
709	0.36	0.36
729	0.48	0.85
750	1.46	1.55
768	3.19	2.57
788	4.62	4.47

The rate of increase of pressure is measured in the first few seconds after the introduction of carbon dioxide. The results should be equal to the rates of reaction at the pressures of carbon dioxide introduced, less corrections for the following factors. The pressure of the carbon dioxide is lowered by the initial transfer of oxygen to the surface, and the carbon monoxide so formed reduces the rate of increase of pressure both by its adsorption and by the consequent retardation. Now the cor-

reactions for all these factors tend to zero as the initial pressure is reduced; the rate of reaction, divided by the initial pressure of carbon dioxide and extrapolated to zero value of the latter, should thus be equal to the constant k_1 of equation (1). Table 3 shows that the values so obtained are in reasonable agreement with those determined by the flow method.

(3) Summary of conclusions

The experimental results can now be summarized and the rates of the individual stages of the reaction calculated from the measurements made by the flow method. The experiments with the static apparatus suggest that the important steps are the following:



The retardation by carbon monoxide is due to the adsorption of the gas on the reaction sites, which represent about 0.5 % of the total surface of the charcoal. Assuming that the sites are equivalent, independent and each capable of adsorbing one atom of oxygen or one molecule of carbon monoxide, it can be shown (Gadsby *et al.* 1946) that the rate of reaction in the steady state is given by

$$\text{rate} = \frac{i_1 p_{\text{CO}_2}}{1 + \frac{i_2 p_{\text{CO}}}{j_2} + \frac{i_1 p_{\text{CO}_2}}{j_3}}. \quad (11)$$

Equation (11) is of the same form as the rate expression, equation (1), and is thus consistent with the results of the flow experiments. If the constants in equation (11) are identified with the corresponding ones in equation (1), the following values are obtained for the rates of the individual stages of the reaction:

$$i_1 = k_1 = 10^{8.8 \pm 0.6} e^{-58,800 \pm 2,600/RT} \text{ g.mol. min.}^{-1} \text{ atm.}^{-1} \text{ g.}^{-1}, \quad (12)$$

$$j_3 = k_1/k_3 = 10^{2.3 \pm 0.9} e^{-28,700 \pm 4,400/RT} \text{ g.mol. min.}^{-1} \text{ g.}^{-1}, \quad (13)$$

$$i_2/j_2 = k_2 = 10^{-7.9 \pm 0.7} e^{+45,500 \pm 3,500/RT} \text{ atm.}^{-1}. \quad (14)$$

The exponential terms in equations (12) and (13) give the activation energies of the corresponding processes. That in equation (14) represents the difference between the activation energies for adsorption and desorption, and thus the energy given out when carbon monoxide is adsorbed on the reaction sites.

To interpret the results on the basis of the alternative retardation mechanism (equation (27) Gadsby *et al.* 1946) would lead to the impossible activation energy of -17 kcal. for the reaction of carbon monoxide with adsorbed oxygen to reform carbon dioxide. The explanation of the retardation as due to the adsorption of carbon monoxide is thus to be preferred on energetic as well as on other grounds.

The fact that the net energy required for the evaporation of carbon monoxide (46 kcal.) is greater than the observed activation energy (29 kcal.) for the conversion of adsorbed oxygen into gaseous carbon monoxide supports the distinction between adsorbed oxygen and adsorbed carbon monoxide.

DISCUSSION

It is shown below that the main features of the reaction can be interpreted on the basis of simple theoretical principles. The general conclusions are compared with those reached by Semchikova & Frank-Kamenetzky (1940) about the reaction of carbon dioxide with sugar charcoal.

The active sites. It is reasonable to suppose that the active sites consist of some of the less firmly bound carbon atoms, since the latter are best situated, not only to form the required bonds with oxygen or carbon monoxide, but also subsequently to detach themselves from the rest of the solid. Many of the surface atoms, as, for example, those in the middle of a layer of the graphite structure, must be exerting their full valency in combination with neighbouring atoms. In a micro-crystalline material, however, such lattice planes are of limited extent, and at their edges atoms forming fewer bonds will be found. If some of these are thought to be the active ones, the fact that they represent only a fraction of the total surface finds a natural explanation in terms of the structure of the charcoal.

The first stage of the reaction. In the initial reaction of the carbon dioxide molecule with the surface an atom of oxygen is adsorbed and a molecule of carbon monoxide passes into the gas phase. It might have been expected, however, that the oxygen and the carbon monoxide would be adsorbed simultaneously. Carbon monoxide itself can be adsorbed alone, and the exothermicity of the change (46 kcal.) might well have facilitated the dissociation of the carbon dioxide; the fact that the active sites are those which do adsorb carbon monoxide strongly would also have been explained. Unless the special assumption that each active carbon atom is surrounded only by inactive ones is made, the experimental result implies that the carbon monoxide does not come into direct contact with the carbon, and consequently that the process takes place in an end-on collision of the carbon dioxide molecule with the surface. The simultaneous adsorption of the oxygen and the carbon monoxide would clearly require a broadside-on collision. That the end-on configuration is, in fact, the most favourable one for reaction is suggested by the work of Buschmann & Schäfer (1941) on the dispersion of supersonic waves in carbon dioxide. It was found that translational energy is more readily transferred to the valency than to the deformation vibrations of the molecule. It is reasonable to suppose, therefore, that the end-on collisions are the most favourable for the conversion of translational energy into vibrational energy, and thus for the disruption of the molecule on reaction.

The order of magnitude of the rate of this stage of the reaction can be accounted for theoretically as follows. It will be assumed that the change occurs when a carbon

dioxide molecule collides with an active site, provided that energy greater than E^* is available. For this purpose no allowance need be made, at least to a first approximation, for the possible effect of orientation. The nature of the process suggests that the activation energy may be shared between the translational motion of the carbon dioxide, the internal vibrations of the molecule and the vibration of the carbon atom to which the oxygen is transferred. It can be shown that the rate at which molecules of mass m and translational energy greater than E collide with a surface of area A is equal to

$$\frac{Ap(1 + E/RT)e^{-E/RT}}{(2\pi mkT)^{\frac{1}{2}}},$$

where p is the pressure of the gas. A standard method (e.g. Fowler & Guggenheim 1939, p. 497) then gives for the rate of reaction, when the activation energy E^* is shared between the translational motion and s modes of vibration,

$$\frac{Ap e^{-E^*/RT} s+1}{(2\pi mkT)^{\frac{1}{2}}} \sum_{r=0}^{\infty} \frac{1}{r!} \left(\frac{E^*}{RT} \right)^r.$$

Here E^*/RT , which is of the order of 30, is much greater than $s+2$, and thus a good approximation is

$$\text{rate} = \frac{Ap}{(2\pi mkT)^{\frac{1}{2}} (s+1)!} \left(\frac{E^*}{RT} \right)^{s+1} e^{-E^*/RT}. \quad (15)$$

Since the experimental results have been represented by an expression of the form

$$\text{rate} = k_{01} p_{\text{CO}_2} e^{-E_1/RT}, \quad (16)$$

the true activation energy E^* should be equal to $E_1 + (s + \frac{3}{2}) RT$, and the theoretical value of the non-exponential factor should be given by

$$k_{01} = \frac{A}{(2\pi mkT)^{\frac{1}{2}} (s+1)!} \left(\frac{E_1 + (s + \frac{3}{2}) RT}{RT} \right)^{s+1} e^{-(s+1)}. \quad (17)$$

The value of s is taken to be 3, since the vibration of the carbon atom perpendicular to the surface and the two valency vibrations of the carbon dioxide are the modes which might reasonably be expected to contribute to the activation energy. A , the total effective area of the active sites, is assumed on the basis of the adsorption measurements to be 0.5 % of the total surface and thus to be $1.5 \times 10^4 \text{ cm}^2 \text{ g}^{-1}$. For E_1 the experimental value of 59 kcal. is substituted; as the mean temperature of the measurements is 782°C , E^* is equal to 68 kcal. If the result is expressed in $\text{g.mol. min}^{-1} \text{ atm}^{-1} \text{ g}^{-1}$, the calculated value of k_{01} becomes $10^{8.0}$ which is to be compared with the observed value of $10^{8.8 \pm 0.6}$. The agreement obtained suggests that the rate of reaction is determined mainly by the energetic considerations outlined above, and can thus be understood in terms of familiar kinetic principles.

The second stage of the reaction. General theory suggests that the rate at which adsorbed oxygen forms gaseous carbon monoxide should be represented approximately by the expression

$$j_3 = \nu e^{-E_1/RT}. \quad (18)$$

The quantity ν is the frequency of the appropriate vibration, and $e^{-E_1/RT}$ is the chance that the required energy is available; n represents the amount of carbon

monoxide equivalent to the total number of active sites, because j_3 relates the rate of reaction to the fraction of the sites occupied. Since the observed activation energy of 29 kcal. is equal to $E_1 - E_3$, it is probable, in view of the correction made to E_1 , that $E^\ddagger$ is greater by $(s + \frac{3}{2}) RT$ and is thus equal to 38 kcal. The frequency ν should consequently be calculated from the relation

$$\nu = j_{03} e^{(s+\frac{3}{2})/n}. \quad (19)$$

On substituting the observed value of the non-exponential factor j_{03} recorded in equation (13), and the experimental value of 1.5×10^{-5} g.mol. g.⁻¹ for n , it is found that ν is equal to $10^{7.3 \pm 0.9}$ sec.⁻¹.

A simple kinetic treatment of the evaporation of solids (Frenkel 1946, p. 1) identifies ν with the frequency of the free vibrations performed by the surface atoms, which is presumably about 10^{13} sec.⁻¹. The application of the transition state theory to evaporation (Glasstone, Laidler & Eyring 1941, p. 354) gives the factor kT/h , which is also of the order of 10^{13} sec.⁻¹ at the temperatures under discussion. The calculations of Polanyi & Wigner (1928) and of Slater (1939) suggest that, in general, when one particular bond must be broken for reaction to occur, ν should be of the same order of magnitude as the frequency of the normal vibrations. Thus, although the experimental value is not a very accurate one, it would seem that some factor tending to reduce the rate of reaction remains to be taken into account. Low probabilities of reaction are often due to the necessity for a transition between two different types of electronic state. Another possible explanation may lie in the fact that the carbon atom carrying the oxygen atom is probably attached to at least two neighbouring carbon atoms. More than one bond must therefore be broken, and a relatively rare coincidence of the phases of a considerable number of vibrations might consequently be required.

The retardation by carbon monoxide. The conclusion that the retardation is due to the adsorption of carbon monoxide is supported by the observed variation of k_2 with temperature. From the latter it is deduced that the heat of adsorption is 46 kcal., while theoretically a large energy change of this magnitude, which implies the formation of a chemical bond with the surface, is required for the gas to be strongly adsorbed. The problem of why the sites which react with carbon dioxide should necessarily take up carbon monoxide is discussed in the next paper; here it will be shown that, given the experimental heat of adsorption, k_2 is of a theoretically reasonable order of magnitude.

The kinetic derivation of the Langmuir isotherm leads to the expression

$$\theta = \frac{\frac{i_2}{j_2} p}{1 + \frac{i_2}{j_2} p} \quad (20)$$

for the fraction (θ) of the active sites occupied at a given pressure (p), where i_2 and j_2 are the rate constants for adsorption and desorption respectively. As k_2 has

already been identified with the ratio i_2/j_2 (equation (14)), it should thus be equal to the characteristic constant of the Langmuir isotherm. Statistical mechanics gives for the non-exponential part of the constant

$$k_{02} = \frac{h^3}{(2\pi mkT)^{3/2}} \frac{h^2}{8\pi^2 I kT} \frac{f_v(\text{ads.})}{f_v(\text{gas.})}, \quad (21)$$

where m is the mass and I the moment of inertia of the carbon monoxide molecule, h is Planck's constant and f_v is the vibrational partition function (Fowler & Guggenheim 1939, p. 427). The product of the vibrational partition functions is unlikely to differ from unity by much more than a factor of 10 and is thus not a very important term; it can, with sufficient accuracy, be written $(1 - e^{-h\nu_a/kT})^{-5}$. The frequency of the isolated molecule is assumed to be unchanged on adsorption and the five additional frequencies are given an average value, ν_a , of 1000 cm^{-1} . Since the increase of the vibrational term and the decrease of the other terms with temperature roughly cancel, no correction is made for the temperature dependence of k_{02} . If the result is expressed in atm^{-1} , the calculated value of k_{02} becomes $10^{-10.1}$, which is roughly similar to the observed value of $10^{-7.9 \pm 0.7}$. The measure of agreement obtained provides further support for the proposed mechanism of reaction.

Comparison with previous work. The reaction of carbon dioxide with pure sugar charcoal, with sugar charcoal containing iron and aluminium and with coke has been studied by Semechkova & Frank-Kamenetzky (1940), who used the static method. The fact that the behaviour of all these materials was found to follow a rate expression of the same form as equation (1) and could be interpreted by a mechanism similar to that deduced for coconut shell charcoal supports the suggestion of a kinetic scheme characteristic of carbon in general. A detailed comparison with the present investigation reveals, however, a number of features which require further comment.

Although the possibility that only certain sites are active was not mentioned by Semechkova & Frank-Kamenetzky, it is not excluded by their experimental results. The gas adsorbed was estimated to cover an area similar to that found for the total surface by means of methylene blue, but it is now known (e.g. Brunauer 1944, p. 277) that the dye adsorption method usually gives values which are much too low. In the scheme proposed for the reaction mechanism, no distinction was made between adsorbed oxygen and adsorbed carbon monoxide. The effect of carbon monoxide was not, in fact, determined directly, so it was assumed, in order to evaluate the rate constants k_1 and k_3 , that

$$k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2} = k_3 p_{\text{CO}_2}^0, \quad (22)$$

at comparable values of p_{CO} and p_{CO_2} . For coconut shell charcoal from 734 to 829°C , k_2 decreases from 93 to 13 atm^{-1} , while k_3 increases from 1.0 to 3.8 atm^{-1} ; the application of equation (22) would thus lead to erroneous values for the constants. With another type of charcoal, however, the carbon monoxide term might be less important.

For the first stage of the reaction Semechkova & Frank-Kamenetzky found an activation energy of 27 kcal. and a steric factor of 10^{-5} . Since practically identical

values were obtained for all the materials studied, it was argued that the process is not affected by the state of the carbon surface, and therefore that an energy of 27 kcal. possessed solely by the carbon dioxide molecule should invariably be required. The present investigation gives an activation energy of 68 kcal., which is thought to be shared among all the degrees of freedom concerned; moreover, no steric factor need be introduced. There is much greater similarity between the results obtained for the second stage of the reaction. The observed activation energy is 61 kcal. for pure sugar charcoal (0.07 % ash) and 23 kcal. for a sample containing 7 % of iron; the corresponding non-exponential factors are 10^9 and 10^2 sec.^{-1} respectively. This range of values includes the figures of 29 kcal. and 10^7 sec.^{-1} now obtained for a coconut shell charcoal of which the iron content (0.15 %) is intermediate between the above extremes. In view of the marked influence of the impurities, however, it is clear that the satisfactory correlation of the detailed behaviour of different types of carbon must await the elucidation of the fundamental features of the catalysis.

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The mechanism of the steam-carbon reaction

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The detailed mechanism of the reaction between steam and coconut shell charcoal has been studied by the method described in the preceding paper. The temperature has been varied in the range 680 to 800° C and the pressures of the gases from 10 to 760 mm.

Steam first reacts with the carbon to give oxygen and hydrogen atoms separately adsorbed on neighbouring sites. An initial dissociation into an adsorbed hydrogen atom and an adsorbed hydroxyl radical is probably followed by the more rapid transfer of the second hydrogen atom to the carbon. Only about 2% of the total surface takes part in the reaction; these sites are distinct from the smaller group which reacts with carbon dioxide, but they are also thought to be atoms at the edges of lattice planes. The rate of the first stage can be accounted for by assuming that reaction occurs in those collisions in which the combined energy of the incident steam molecule and the two active carbon atoms exceeds 75 kcal. Adsorbed hydrogen evaporates rapidly, but in the steady state much remains on the surface. A close correlation has been observed between the fraction of the active sites occupied by hydrogen and the extent to which the reaction is retarded by that gas. Adsorbed oxygen reacts much more slowly to form gaseous carbon monoxide; the latter, which has no retarding effect, is not appreciably adsorbed by the sites accessible to steam. The activation energy for the conversion of an adsorbed oxygen atom into gaseous carbon monoxide is found to be 55 kcal., and the non-exponential factor to be $10^{11.3 \pm 1.7} \text{ sec.}^{-1}$ which may be compared with the value of $10^{13} \text{ sec.}^{-1}$ predicted by simple theory.

As the active carbon atoms are thought to be exerting less than their maximum valency, it is suggested that the two types differ in the number of extra bonds which they can form. Energetic considerations show that whereas those which can form a single bond should react with steam, only the relatively few capable of forming a double bond should react with carbon dioxide. This theory also explains why hydrogen is strongly adsorbed by both the steam and the carbon dioxide sites, but carbon monoxide only by the latter type.

The relation of these views to outstanding problems of the oxygen-carbon and nitrous oxide-carbon reactions is discussed, and an explanation of the main kinetic features of those processes is given.

INTRODUCTION

It has previously been shown (Gadsby, Hinshelwood & Sykes 1946) that carbon monoxide is the primary product of the action of steam on charcoal, and that the rate of reaction depends on the partial pressures of steam and hydrogen according to the relation

$$\text{rate} = \frac{k_1 p_{\text{H}_2\text{O}}}{1 + k_2 p_{\text{H}_2} + k_3 p_{\text{H}_2\text{O}}} \quad (1)$$

In the present paper an investigation of the detailed mechanism of the process is described. The method is analogous to that explained in the preceding paper on the carbon dioxide reaction; the adsorption of the gases is studied by the static technique and the variation of the rate of reaction with temperature is measured by the flow technique. In the discussion an attempt is made to account for the mechanisms of both the steam and carbon dioxide reactions by the same fundamental considerations.

EXPERIMENTAL TECHNIQUE

The improved flow apparatus in which the spatial distribution of temperature is controlled automatically is used without further change.

In the static apparatus provision is made to introduce a known amount of steam and to analyze the resulting gaseous mixture. Each experiment is made with 10 g. of charcoal in a reaction vessel of volume 290 c.c. Water, freed from dissolved air by repeated freezing and evacuation, is vaporized into a storage vessel immersed in an oil thermostat at 75° C and fitted with a mercury manometer; the decrease in pressure of the latter measures the amount of steam subsequently transferred to the reaction vessel. All manometers and other tubing outside the thermostat are kept at about 80° C by electrical heating. Trial experiments in the absence of charcoal showed that up to 260 mm. of steam could be admitted to the storage vessel and shared to give 170 mm. in the reaction vessel without detectable condensation. Gas samples are withdrawn through a phosphorus pentoxide tube into an evacuated receiver. The total amount of gas extracted is measured by the decrease of pressure in the reaction vessel; the amount left after the removal of the steam by the phosphorus pentoxide is proportional to the pressure developed in the receiver, which is observed with respect to vacuum by means of a butyl phthalate manometer. By comparison with calibration experiments, in which argon is withdrawn from the reaction vessel, a reasonable estimate of the steam pressure can easily be obtained. The remaining mixture of hydrogen, carbon monoxide and carbon dioxide is analyzed with a Haldane apparatus.

All other features of the experimental technique are as described in the preceding paper. Since it has been shown that the carbon dioxide reaction is not appreciably affected by diffusion in either the flow or the static experiments, it will be assumed that under similar conditions the same is true for the steam reaction, the rate of which is of the same order of magnitude.

RESULTS

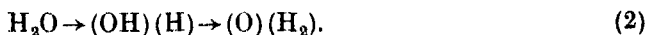
(1) *The static method**The course of reaction*

Figure 1 illustrates the results of a series of experiments in which the same amount of steam is allowed to remain in contact with the charcoal for a series of different times; the curves are typical of those obtained at pressures of 50 to 150 mm. in the temperature range 700 to 800° C. In the upper part of the figure the partial pressures of the gases are plotted against time. The initial pressure, $p_{\text{H}_2\text{O}}^0$, is the pressure which the steam would exert if neither adsorption nor reaction occurred, and is calculated, on the basis of calibration experiments with argon, from the amount of steam introduced. The lower part of the figure shows the corresponding changes in the amounts of oxygen and hydrogen adsorbed, taken respectively to be

$$p_{\text{H}_2\text{O}}^0 - (p_{\text{H}_2\text{O}} + p_{\text{CO}} + 2p_{\text{CO}_2}) \quad \text{and} \quad p_{\text{H}_2\text{O}}^0 - (p_{\text{H}_2\text{O}} + p_{\text{H}_2}).$$

The amounts adsorbed are thus expressed as the pressures which they would exert in the gas phase, the hydrogen as such and the oxygen as carbon monoxide. These stoichiometric definitions make no assumptions about the state of the oxygen and hydrogen on the surface, and thus include that present either as steam or in any other form.

At first the pressure falls rapidly as steam is adsorbed. If the steam molecule as such was the only adsorbed species, the amount of oxygen adsorbed would be equal to the amount of hydrogen adsorbed throughout the reaction. Figure 1 shows, however, that the two quantities are by no means equal and that they vary with time in entirely different ways. Although it is clear that much of the surface is covered by hydrogen in the later stages, the possibility of explaining the results in terms of steam and hydrogen as the adsorbed species is ruled out by the observation that initially the oxygen is in excess of the hydrogen. It is concluded, therefore, that steam is dissociated into oxygen and hydrogen separately attached to neighbouring sites. This decomposition of the steam molecule may be regarded as a natural result of the fact that adsorption at high temperatures requires the formation of chemical bonds with the surface. The simplest, and consequently the most probable, mechanism is the initial formation of an adsorbed hydrogen atom and an adsorbed hydroxyl radical, followed by the transfer of a hydrogen atom from the hydroxyl to the carbon; the first stage of the reaction may thus be written:



Hydrogen evaporates rapidly, as shown by the sharp initial rise in its partial pressure, but a steady state in which a considerable proportion remains on the surface is soon reached. The continual increase during the later stages in the amount of hydrogen adsorbed for a given partial pressure suggests that this gas progressively occupies the sites left vacant by the reaction of the adsorbed oxygen. It is therefore very probable that the adsorption of hydrogen is the factor which causes the reaction to be retarded by that gas; the suggestion that the adsorption of steam requires its dissociation into oxygen and hydrogen explains why steam and hydrogen compete for the same sites. The part played by hydrogen can thus be expressed by writing:



The adsorbed oxygen leaves the surface much more slowly, as can be seen from the relative pressures of carbon monoxide and hydrogen during the first few minutes. In the end, however, it is almost completely converted into gaseous carbon monoxide, together with a small proportion of carbon dioxide, and the amount adsorbed falls to less than 2 mm. Figure 9 of the preceding paper shows that when carbon monoxide is present alone, at a pressure of 62 mm., the final value reached in figure 1, the amount adsorbed is 12 mm. It must thus be supposed that the sites which normally take up carbon monoxide are now preferentially occupied by hydrogen. The fact that under the present conditions carbon monoxide has little tendency to return to the surface explains the observation (Gadsby, Hinshelwood & Sykes 1946) that this

gas does not retard the steam reaction. The results also support the previous conclusion that the carbon dioxide is formed secondarily from carbon monoxide and steam. At these pressures the latter reaction is of approximately the first order with

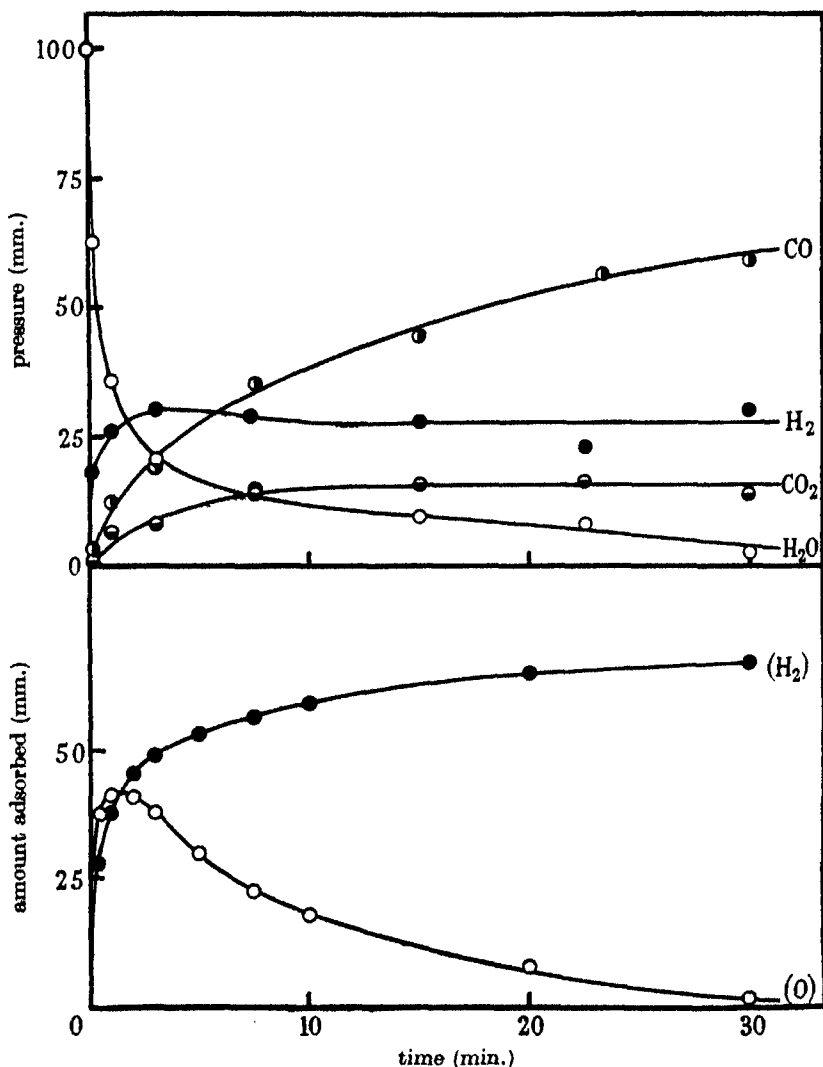


FIGURE 1. The course of reaction at an initial steam pressure of 100 mm. at 750° C: partial pressures in the gas phase and adsorption on the carbon surface.

respect to each gas, so the proportion of carbon dioxide rises as the pressure of carbon monoxide increases and then falls on account of the decrease in the steam pressure. The remaining stage of the reaction can thus be represented by the equation



It can be shown that the mechanism proposed above is consistent with the dependence of the amounts adsorbed during the course of the reaction on temperature and pressure. The changes which occur when steam is introduced at a

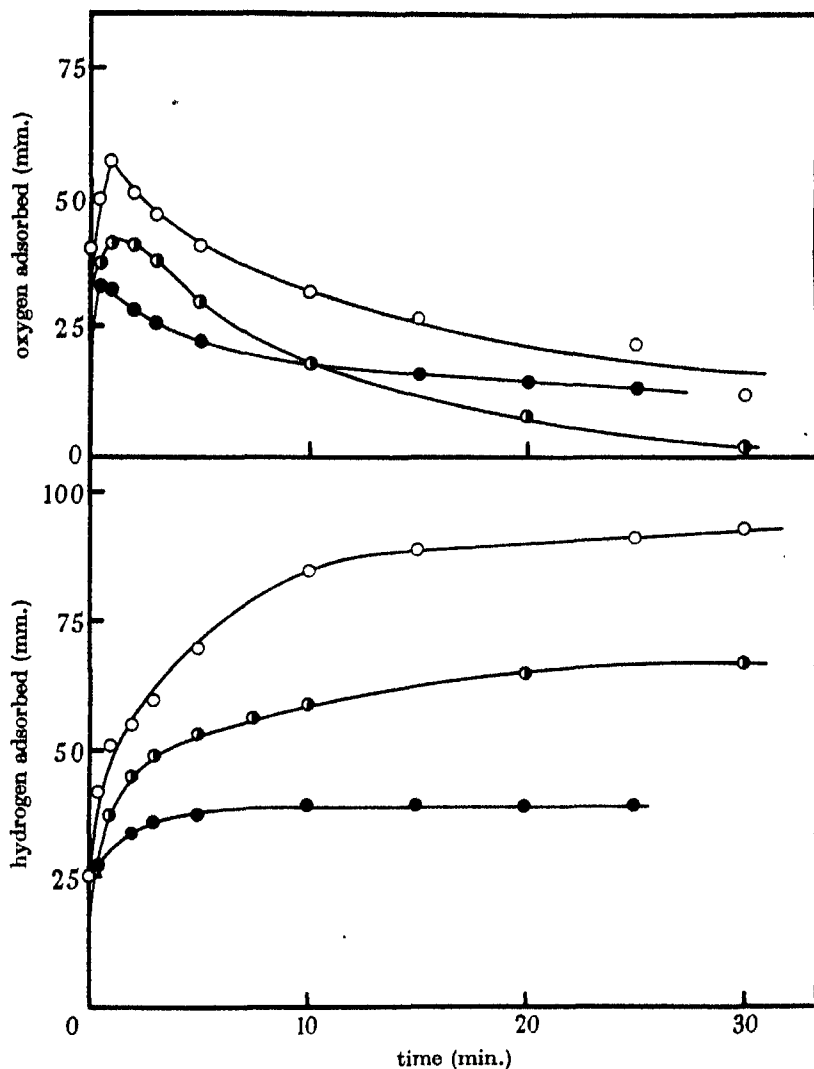


FIGURE 2. Adsorption on the carbon surface during reaction at a series of different steam pressures at 750° C. Initial pressure of steam: ○ 150 mm.; ◐ 100 mm.; ● 55 mm.

series of different pressures are illustrated in figure 2, where the amounts of oxygen and hydrogen found on the surface are plotted against time in the upper and lower portions of the diagram respectively. Both these quantities increase as the initial pressure is raised, the hydrogen almost proportionally and the oxygen to a slightly

smaller extent. Such variations are to be expected, since the reaction is of nearly the first order with respect to steam at these pressures and is progressively retarded as the pressure of hydrogen is increased.

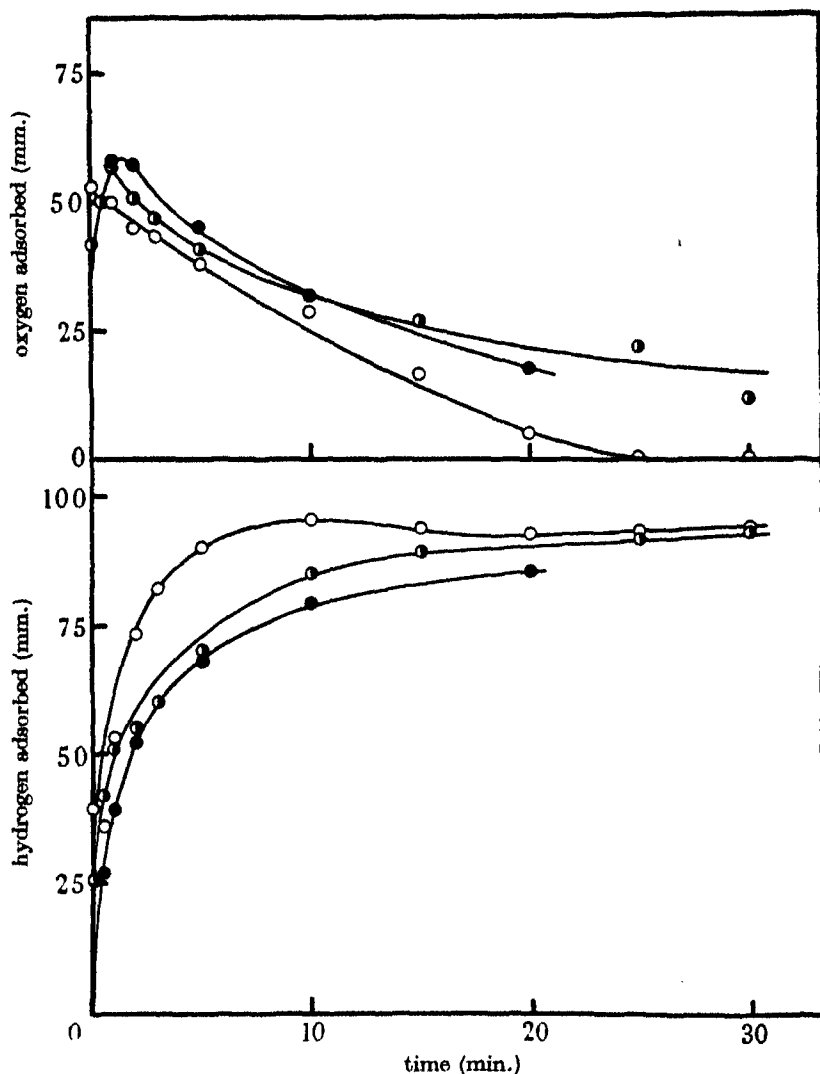


FIGURE 3. Adsorption on the carbon surface during reaction at a series of different temperatures. Initial steam pressure 150 mm. ○ 800° C; ◐ 750° C; ● 700° C.

Figure 3 shows, in a similar way, the effect of introducing a given pressure of steam at a series of different temperatures. Although an increase of temperature from 700 to 800° C raises the initial rate of adsorption, it does not alter very markedly the amounts on the surface during the greater part of the reaction. However, when

allowance is made for the decrease of the overall pressure of steam caused by the increase in the rate of reaction, the amount of oxygen adsorbed for a given pressure of steam is found to be greater the higher the temperature. This conclusion is in good agreement with the flow experiments, which yield a higher activation energy for the initial transfer of oxygen to the surface (75 kcal.) than for its subsequent evaporation as carbon monoxide (55 kcal.). It can also be seen from figure 3 that the amount of hydrogen finally adsorbed is roughly independent of temperature; this observation is consistent with the lack of variation revealed by the flow experiments in the extent to which the reaction is retarded by hydrogen (k_2 , figure 9).

The adsorption of hydrogen

A known quantity of the gas is introduced, and the difference between the observed pressure and the calculated initial value, which represents the amount adsorbed, is plotted against time in figure 4. No correction need be made for the comparatively slow formation of methane, since even the equilibrium proportion does not exceed 1 % under the present conditions. It is clear that hydrogen itself is strongly adsorbed at a rate similar to that of steam, as required by the proposed mechanism of reaction. The typical carbon monoxide curve, which is included for comparison, emphasizes that this latter gas combines with the charcoal, not only much less rapidly, but also to a considerably smaller extent.

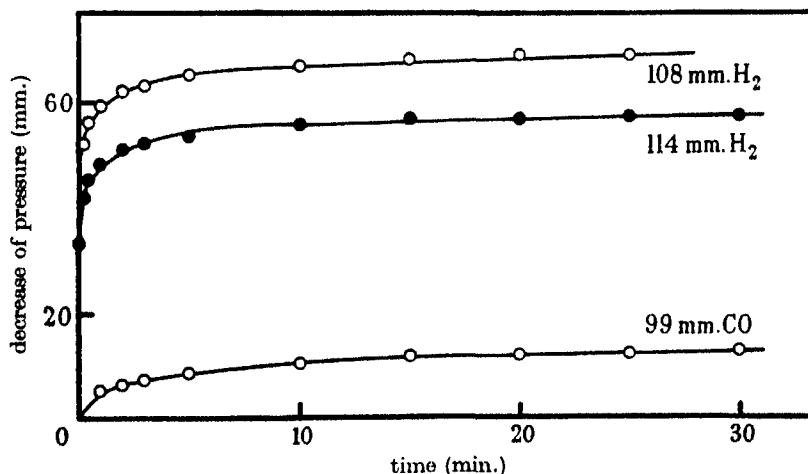


FIGURE 4. The rate of adsorption of hydrogen. ○ 800° C; ● 750° C.

In figure 5 the amount of hydrogen adsorbed after a period of 20 min. is plotted against the pressure of that remaining in the gas phase. Although during this time the rate of adsorption falls to a very small fraction of its initial value, equilibrium is not reached. For the present purpose, however, the subsequent changes can be neglected because they are too slow to play any appreciable part in the reactions

under consideration. To show that the experimental points can be represented adequately by the Langmuir isotherm, the curves are calculated from the equation

$$\text{amount adsorbed} = q = \frac{q_0 b p_{\text{H}_2}}{1 + b p_{\text{H}_2}}. \quad (5)$$

The values of the constants q_0 and b , which are obtained from the straight line drawn by the method of least squares on the graph of p_{H_2}/q against p_{H_2} , are recorded in table 1; the probable errors are calculated from the residuals in the usual way.

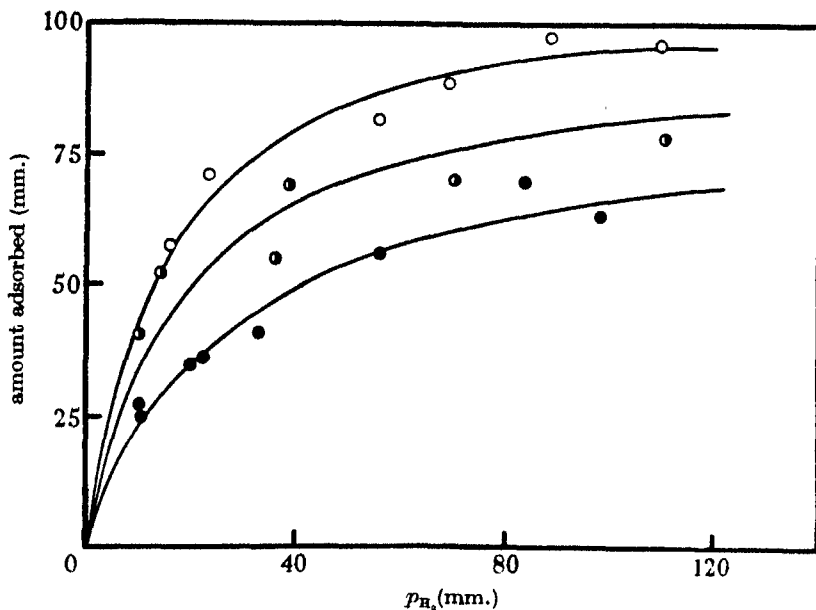


FIGURE 5. The amount of hydrogen adsorbed. Comparison of experimental points with curves calculated according to equation (5) from the values of the constants given in table 1. $\circ$ 850° C; $\bullet$ 800° C; $\bullet$ 750° C.

TABLE 1

temp. (° C)	q_0 (g.mol. g. ⁻¹ × 10 ⁵)	b (atm. ⁻¹)
750	3.8 ± 0.2	27 ± 3
800	4.0 ± 0.2	42 ± 8
850	4.5 ± 0.1	50 ± 7

For a given pressure of hydrogen, the amount adsorbed under these conditions is about 90 % of that found on the surface during the steam reaction. There, however, equilibrium is approached from the other side, as the hydrogen is originally formed in the adsorbed state. The quantity q_0 represents the limiting amount adsorbed at high pressures and is thus a measure of the total number of sites available. It tends to increase slightly as the temperature is raised, but is roughly equal to 4×10^{-5} g.mol./g. of charcoal. The pronounced curvature of the isotherms suggests that the

hydrogen adsorbed at these pressures occupies a considerable fraction of the active surface, and is consequently capable of causing the observed retardation. As the adsorption of a gas is accompanied by a marked decrease of entropy, the process will take place to an appreciable extent at high temperatures only if it is strongly exothermic; the constant b , which is a measure of the tendency for adsorption, should thus decrease exponentially as the temperature is raised. Here, however, b tends to vary in the opposite sense, so it must be supposed that a true steady state is not established. This explanation is supported by the work of Barrer (1935), who discovered that the time required for equilibrium to be reached is as long as 2 or 3 days; from the temperature dependence of the results so obtained, the heat given out on adsorption was calculated to be 50 kcal. The magnitude of this value shows clearly that the strong adsorption of the hydrogen molecule is due to its dissociation into atoms, each of which forms a chemical bond with a previously unsaturated carbon atom. Barrer also found that only a small fraction of the total surface is involved, and that the Langmuir isotherm is obeyed; another paper (Barrer 1936*a*) discusses the conditions under which adsorption with dissociation leads to an isotherm of this type.

The active sites

Carbon dioxide was found to react not with the whole of the charcoal surface, but only with certain active sites representing about 0.5 % of the total area. The properties attributed to those sites will not, however, account for the results described above. For example, carbon monoxide retards the action of carbon dioxide by being strongly adsorbed and yet has no appreciable effect on that of steam. It is concluded that steam reacts predominantly with a different type of site, which evidently has little tendency either to take up carbon monoxide or to be attacked by carbon dioxide. Hydrogen, of which up to 4×10^{-5} g.mol. g.⁻¹ can be adsorbed as compared with only 1.5×10^{-5} g.mol. g.⁻¹ of carbon monoxide, must be supposed to occupy both groups of sites, in order to explain why the carbon monoxide formed in the steam reaction does not return to the surface to any appreciable extent. This conclusion is supported by the previous observation (Gadsby *et al.* 1946) that the carbon dioxide reaction is retarded by hydrogen as well as by carbon monoxide. Since considerations to be discussed later suggest that one type of site can accommodate either two atoms of hydrogen or a molecule of carbon monoxide and the other only one atom of hydrogen, the above figures lead to an estimate of 3.3 for the ratio of the numbers of sites in the two separate groups.

If a given fraction of one set of sites is occupied during the steam reaction, then approximately the same fraction of the other set should be occupied under analogous conditions in the carbon dioxide reaction; this conclusion follows from the similarity of the kinetic expressions. The maximum values of the total amounts of gas adsorbed in the course of the two reactions are compared in table 2.

These quantities are not equal to each other, but the last column shows that their ratio is roughly independent of both temperature and pressure; they can thus be

considered to represent similar fractions of two different groups of sites. The average value of the ratio recorded in table 2 being 4.3, roughly 3.3 g.mol. are adsorbed on the steam sites for every 1 g.mol. adsorbed on the carbon dioxide sites. Since about half the former amount consists of hydrogen, one molecule of which requires two sites, the carbon atoms accessible to steam appear to outnumber those accessible to carbon dioxide by a factor of 5.0. Comparison with the estimate of 3.3, obtained above, suggests that the correct value is about 4, so it is concluded that the sites which react specifically with steam account for approximately 2 % of the charcoal surface.

TABLE 2

temp. (° C)	initial pressure (mm.)	total amount adsorbed		ratio
		H ₂ O reaction (mm.)	CO ₂ reaction (mm.)	
800	150	128	38	3.6
750	150	123	26	4.7
700	150	113	32	3.5
750	100	87	21	4.1
750	55	65	12	5.4

(2) *The flow method**The rate of reaction*

Measurements are made at five temperatures in the range 680 to 770° C. The variation of the rate of reaction with the partial pressure of steam is determined by passing through the charcoal column a series of steam-nitrogen mixtures, the total rate of flow being kept constant at 1200 c.c./min. Since carbon dioxide is formed secondarily from carbon monoxide and steam, the rate of the primary process is taken to be the sum of the rates at which the two oxides are produced. To study the effect of hydrogen, various small partial pressures of it are added, the partial pressure of steam and the total rate of flow being kept constant as before. Neither carbon monoxide nor carbon dioxide has any appreciable effect on the rate of this reaction, and the partial pressure of the latter gas is insufficient for its reaction with the charcoal to be significant. Typical results are illustrated in figure 6, where the rate of reaction per gram of charcoal is plotted against the initial pressures of steam and hydrogen.

It can be shown that the expression

$$\text{rate} = \frac{k_1 p_{\text{H}_2\text{O}}}{1 + k_2 p_{\text{H}_2} + k_3 p_{\text{H}_2\text{O}}} \quad (1)$$

is closely obeyed over the whole temperature range. If the conditions (i) to (iii) enumerated in the preceding paper are fulfilled, and if in addition $k_2 p_{\text{H}_2}^0 \gg 1$ and $p_{\text{H}_2\text{O}}^0 > p_{\text{H}_2}^0$, equation (1) leads to the relation

$$\frac{m}{x} = \frac{1 + k_1 p_{\text{H}_2\text{O}}^0}{k} + \frac{k_3 \bar{p}_{\text{H}_2}}{k} \quad (6)$$

The quantity x is now the fraction of steam reacting directly with the charcoal and $\bar{p}_{\text{H}_2}$ is the average partial pressure of hydrogen, including that formed from carbon monoxide and steam; m and k retain their previous definitions. In the present experiments the total rate of flow does not vary by more than 6 %, the rates of diffusion lie between 0.1 and 20 % of the rates of flow, while x , which is rarely greater than 0.10, never exceeds 0.20; the average value of $k_2 p_{\text{H}_2\text{O}}^0$ is about 15 and $p_{\text{H}_2\text{O}}^0/\bar{p}_{\text{H}_2}$ is not less than 1.4. The conditions under which equation (6) is applicable are thus fulfilled to a close approximation.

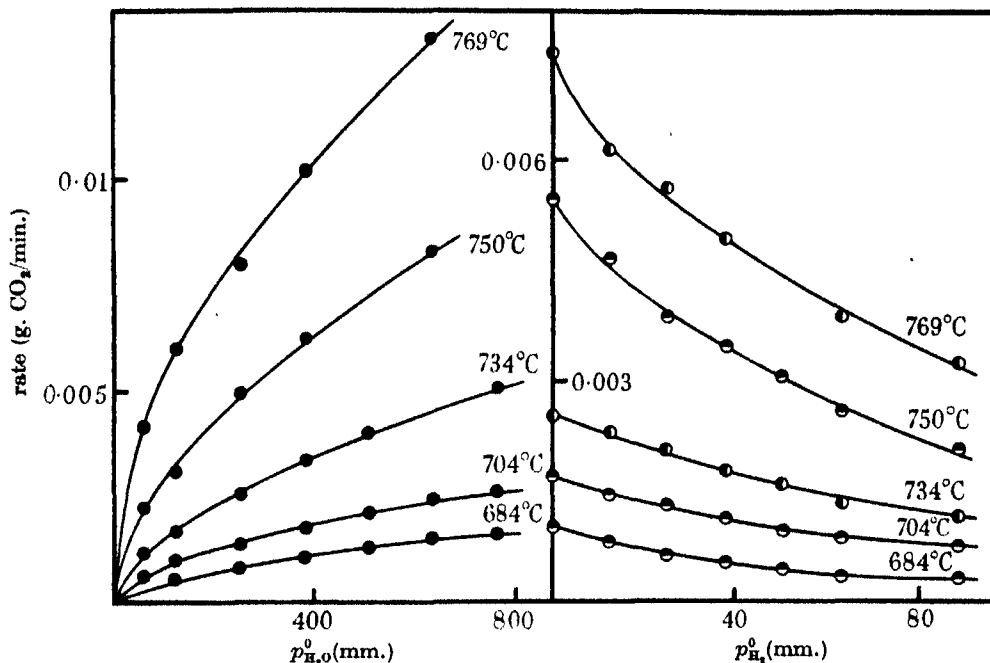


FIGURE 6. Apparent order of reaction with respect to steam and retardation by hydrogen. Initial pressure of steam: $\bullet$ 380 mm.; $\circ$ 253 mm.

Figure 7 shows that the straight lines required by equation (6) are obtained when m/x is plotted against $\bar{p}_{\text{H}_2}$. The relatively small variations of the slope at any given temperature do not depend systematically on $p_{\text{H}_2\text{O}}^0$, and are probably due to lack of complete reproducibility from one experiment to another. In figure 8 the intercept m/x_0 at $\bar{p}_{\text{H}_2} = 0$ is plotted against $p_{\text{H}_2\text{O}}^0$; these intercepts are calculated by subtracting $k_2 \bar{p}_{\text{H}_2}/k$ from the values of m/x obtained in the experiments in which hydrogen is not added. It can be seen that the effect of varying the steam pressure is adequately represented by the linear relation

$$\frac{m}{x_0} = \frac{1 + k_2 p_{\text{H}_2\text{O}}^0}{k}, \quad (7)$$

which follows from equation (6).

Values of the constants and their probable errors are calculated by the method of least squares in the manner described previously. The logarithms of k_1 , k_2 and k_3 are plotted against the reciprocal of the absolute temperature in figure 9, where the radii of the circles are equal to the probable errors. The variation of k_1 approximates

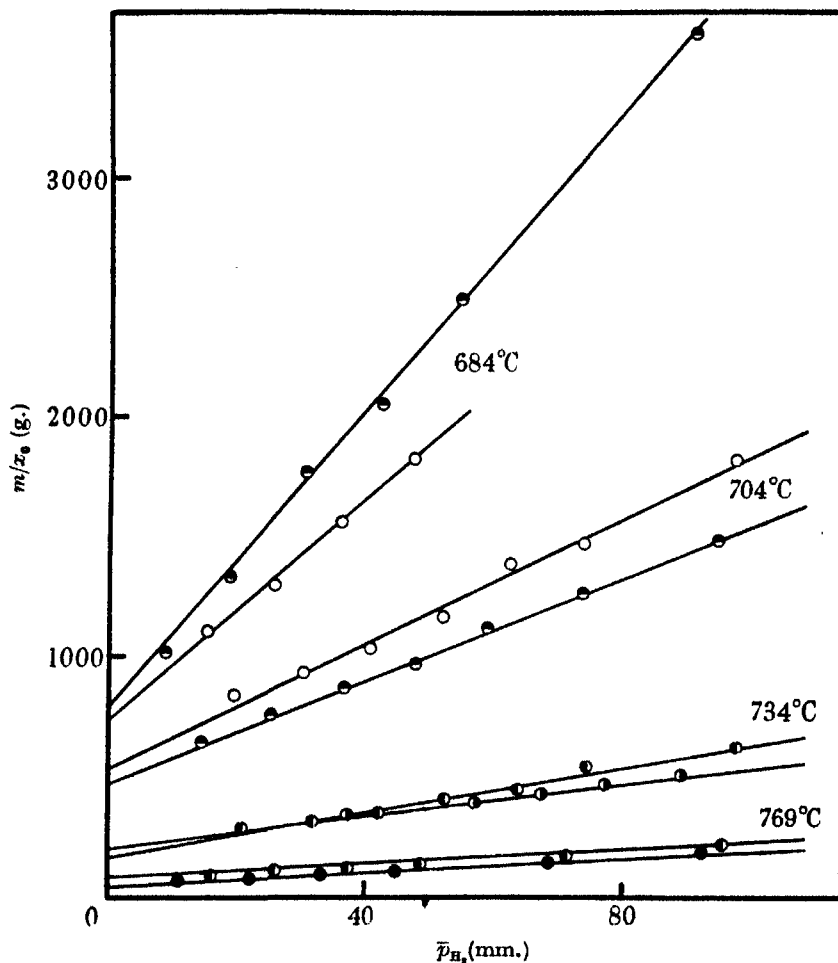


FIGURE 7. Test of rate expression: variation of hydrogen pressure. Initial steam pressure: ○ 633 mm.; ● 506 mm.; ● 380 mm.; ● 253 mm.; ● 127 mm.

closely to an exponential increase with temperature. Although there is no doubt that k_3 also increases as the temperature is raised, the probable errors are larger and the points are consequently more scattered; a straight line has, however, been drawn by the method of least squares. The values of k_2 do not show any significant change. A concise summary of the results may thus be given as follows:

$$\begin{aligned}
 k_1 &= k_{01} e^{-E_1/RT}, \quad \text{where } k_{01} = 10^{10.2 \pm 0.9} \text{ g.mol. min.}^{-1} \text{ atm.}^{-1} \text{ g.}^{-1}, \\
 &\quad \text{and } E_1 = 62.3 \pm 4.1 \text{ kcal. g.mol.}^{-1}; \\
 k_2 &\simeq 33 \text{ atm.}^{-1}; \\
 k_3 &= k_{03} e^{-E_3/RT}, \quad \text{where } k_{03} = 10^{4.5 \pm 1.4} \text{ atm.}^{-1}, \\
 &\quad \text{and } E_3 = 20.1 \pm 6.2 \text{ kcal. g.mol.}^{-1}.
 \end{aligned}$$

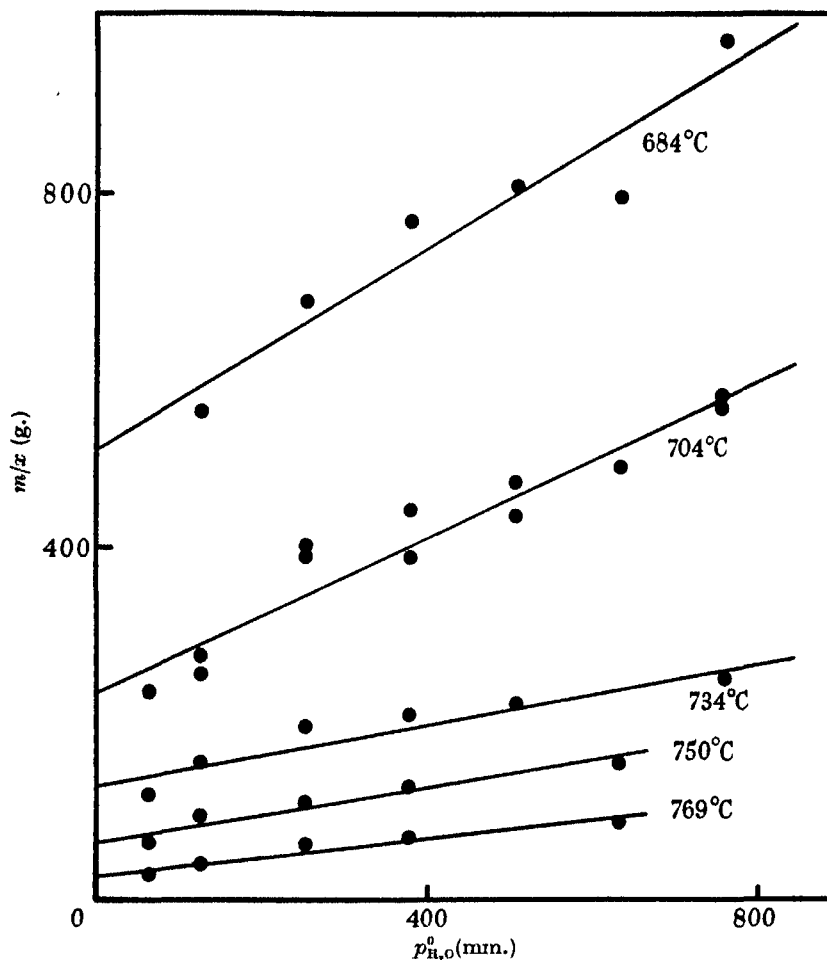
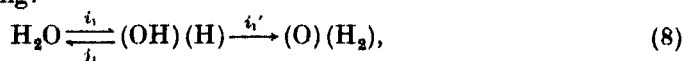


FIGURE 8. Test of rate expression: variation of steam pressure.

The rates of the individual stages

The experiments with the static apparatus suggest that the important elementary processes are the following:



It will be shown below that the retardation by hydrogen can satisfactorily be accounted for by the extent to which the gas is adsorbed; the reverse of the second step in equation (8), which represents an additional way in which hydrogen can

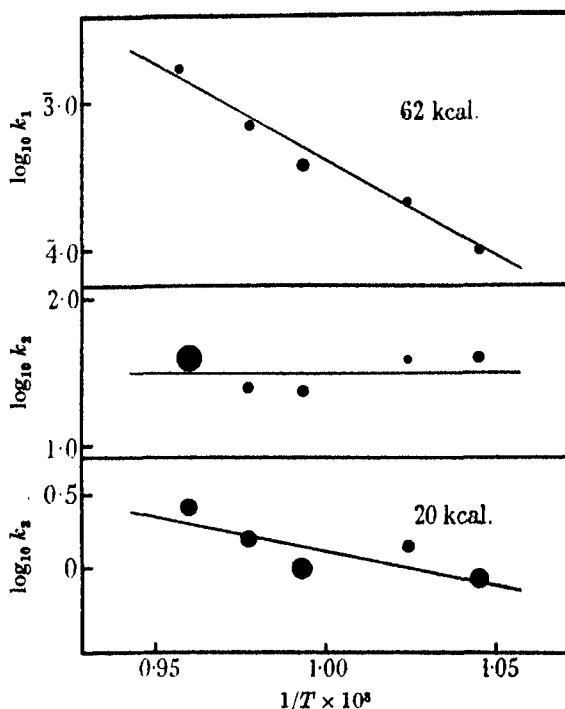


FIGURE 9. Variation of k_1 , k_2 and k_3 with temperature.

reduce the rate of reaction, is thus neglected. The conditions for a steady state may be expressed in general terms by the relations

$$i_1 p_{\text{H}_2\text{O}} (1 - \theta_1 - \theta_2 - \theta_3) = (i'_1 + j_1) \theta_1, \quad (11)$$

$$i_2 p_{\text{H}_2} (1 - \theta_1 - \theta_2 - \theta_3) + i'_1 \theta_1 = j_2 \theta_2, \quad (12)$$

$$i'_1 \theta_1 = j_3 \theta_3, \quad (13)$$

where θ_1 , θ_2 and θ_3 are respectively the fractions of the active surface occupied by (OH) (H), (H_2) and (O). No allowance has been made for the different numbers of sites which the various species require, since this cannot be done without detailed knowledge of the spatial distribution of the active carbon atoms. This approximation is not, however, a very drastic one. The rate of reaction in the steady state is given by

$$\text{rate} = \frac{\frac{i_1 i'_1 p_{\text{H}_2\text{O}}}{i'_1 + j_1}}{1 + \frac{i_2 p_{\text{H}_2}}{j_2} + \left(\frac{1}{i'_1} + \frac{1}{j_2} + \frac{1}{j_3} \right) \frac{i_1 i'_1 p_{\text{H}_2\text{O}}}{i'_1 + j_1}}, \quad (14)$$

which is of the same form as the experimentally determined rate expression, equation (1). It is thus possible to evaluate the rates of some of the individual stages by comparing the corresponding terms in the two expressions.

The numerators yield the relation

$$\frac{i_1 i'_1}{i'_1 + j_1} = k_1. \quad (15)$$

Now Muller & Cobb (1940) found that when charcoal on which steam has been adsorbed at 300° C is heated under vacuum to 1050° C, the steam is not recovered as such but only as hydrogen and oxides of carbon. The results obtained by Strickland-Constable (1947) also show that above 700° C adsorbed steam reacts much more quickly than it evaporates. It follows that under the present conditions j_1 , the rate constant for evaporation of steam, is small compared with i'_1 which refers to an essential step in the comparatively rapid evolution of hydrogen. The rate of the first stage of the mechanism may thus be evaluated by writing equation (15) in the form

$$i_1 = k_1 = 10^{10.2 \pm 0.9} e^{-62,300 \pm 4,100/RT} \text{ g.mol. min.}^{-1} \text{ atm.}^{-1} \text{ g.}^{-1}. \quad (16)$$

The magnitude of the non-exponential factor can be explained by the simple assumption that reaction occurs when a steam molecule collides with an appropriate site, provided that the total energy available is greater than E^* . The theoretical expression

$$k_{01} = \frac{A}{(2\pi mkT)^{1/2} (s+1)!} \left(\frac{E_1 + (s + \frac{3}{2}) RT}{RT} \right)^{s+1} e^{-(s+1)}, \quad (17)$$

which was deduced for the corresponding factor in the carbon dioxide reaction, is applicable here if A is now the area represented by the sites accessible to steam and m is the mass of the steam molecule. Since the vibrations of the two active carbon atoms perpendicular to the surface and the three normal modes of the steam molecule are likely to contribute to the activation energy, the value of s is assumed to be 5. E^* , which is equal to $E_1 + (s + \frac{3}{2}) RT$, thus becomes 75 kcal. A is taken to be $6 \times 10^4 \text{ cm.}^2 \text{ g.}^{-1}$, since it has been found by the static method to represent about 2 % of the total surface area. The value of k_{01} calculated on this basis is $10^{9.8} \text{ g.mol. min.}^{-1} \text{ atm.}^{-1} \text{ g.}^{-1}$, in good agreement with the observed value of $10^{10.2 \pm 0.9}$ in the same units.

Another relation between the constants in equations (1) and (14) is

$$\frac{1}{\frac{1}{i'_1} + \frac{1}{j_2} + \frac{1}{j_3}} = \frac{k_1}{k_3}. \quad (18)$$

The fact that after the adsorption of steam hydrogen is evolved much more rapidly than carbon monoxide implies that both i'_1 and j_2 are large compared with j_3 . Consideration of equations (8) to (10) shows that whichever of i'_1 and j_2 is the smaller should be approximately equal to j_3 multiplied by the ratio of the initial rates of formation of the two gases; reference to figure 1 emphasizes that this ratio is large.

It is thus reasonable to neglect both $1/i_1'$ and $1/j_2$ in comparison with $1/j_3$, and to write equation (18) in the form

$$j_3 = k_1/k_2 = 10^{5.7 \pm 1.7} e^{-42,200 \pm 7,400/RT} \text{ g.mol. min.}^{-1} \text{ g.}^{-1}. \quad (19)$$

This expression for the rate at which adsorbed oxygen atoms evaporate as carbon monoxide may be compared with the theoretical relation

$$j_3 = n\nu e^{-E^\ddagger/RT}, \quad (20)$$

where ν is the appropriate vibration frequency, $E^\ddagger$ the activation energy, and n the amount of carbon monoxide equivalent to the total number of sites available. Since the observed activation energy of 42 kcal. is given by $E_1 - E_3$, the correction of $(s + \frac{3}{2})RT$ applied to E_1 makes $E^\ddagger$ equal to 55 kcal. The quantity n has been estimated to be roughly four times the corresponding figure for the carbon dioxide reaction, and is consequently taken to be $6 \times 10^{-5} \text{ g.mol. g.}^{-1}$. If the observed value of the non-exponential factor j_{03} is now substituted in the relation

$$\nu = j_{03} e^{(s+\frac{1}{2})/n}, \quad (21)$$

the frequency ν is found to be $10^{11.0 \pm 1.7} \text{ sec.}^{-1}$. This value is in reasonable agreement with the figure of $10^{13} \text{ sec.}^{-1}$ predicted by the simple theory outlined in the preceding paper. The fact that the values of $E^\ddagger$ and ν are not the same as those obtained for the analogous stage of the carbon dioxide reaction (38 kcal. and 10^7 sec.^{-1}) can readily be understood in terms of the idea that two distinct groups of sites are involved. Since the observed non-exponential factor is markedly smaller than the theoretical figure only for the carbon dioxide reaction, it is tentatively suggested that the discrepancy is due to a non-adiabatic transition. The other possible explanation of a low-frequency factor mentioned in the discussion of the carbon dioxide results seems unlikely to make the reaction probability depend so specifically on the type of site concerned.

Comparison of the hydrogen retardation terms in equations (1) and (14) implies that

$$i_2/j_2 = k_2 \approx 33 \text{ atm.}^{-1}. \quad (22)$$

As i_2 and j_2 represent respectively the rates of adsorption and desorption, it follows from the kinetic derivation of the Langmuir isotherm (see equation (20) in the preceding paper) that k_2 should be equal to the constant b in equation (5). The observation that the adsorption of hydrogen can be described by an isotherm of this type is thus consistent with the form of the rate expression. It remains, however, to compare the numerical values of k_2 determined by the flow technique with those of b calculated from the static adsorption measurements. Table 1 shows that b is equal to $27 \pm 3 \text{ atm.}^{-1}$ at 750°C and $42 \pm 8 \text{ atm.}^{-1}$ at 800°C ; the values of k_2 observed between 680 and 770°C all lie in the range 23 to 40 atm.^{-1} and their average is 33 atm.^{-1} . Although equilibrium may not be approached to quite the same extent in the two sets of experiments, the reasonable agreement obtained is thought to confirm the conclusion that the retardation caused by hydrogen is due to its adsorption.

DISCUSSION

It is now possible to summarize the main features of the reactions of charcoal with steam and with carbon dioxide, and to see how far they can be interpreted on the basis of general principles.

The mechanisms are fundamentally similar, each overall process taking place in two main stages. A molecule of steam or carbon dioxide is first decomposed by the transfer of an oxygen atom to the carbon surface; the oxygen atom then evaporates, together with an atom of carbon from the solid, to form gaseous carbon monoxide. There is a significant difference of detail between the initial stages of the two reactions, but this can largely be attributed to the different structures of the molecules concerned. Whereas carbon dioxide is decomposed into an atom of oxygen which is adsorbed and a molecule of carbon monoxide which passes into the gas phase, the whole of the steam molecule is taken up by the charcoal. However, the dissociation of carbon dioxide gives an atom with a considerable affinity for carbon and a stable molecule which is itself only slowly adsorbed, while that of steam yields a hydrogen atom and a hydroxyl radical, each of which is expected to combine readily with the carbon.

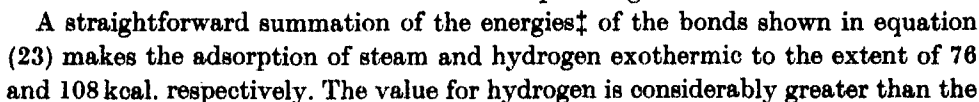
Both steam and carbon dioxide attack only a small fraction of the total surface of the charcoal; this is a natural consequence of the micro-crystalline structure of the material, since a small but by no means negligible proportion of the surface atoms will be situated at the edges of the individual lattice planes, and will therefore be exceptionally reactive on account of their weaker binding to the rest of the solid.

The rates of reaction can also be understood in terms of familiar principles. Given the experimental activation energy and the number of active sites determined by the adsorption measurements, the rate of the first stage of each reaction can be calculated to within the nearest order of magnitude from simple kinetic theory. A similar treatment of the second stage yields theoretical rates which are greater than those observed, but the discrepancy can be ascribed to complicating factors likely to be significant in these reactions.

The more general features of the mechanism outlined above follow in a straightforward manner the tendency for reactions to take place in a series of simple steps, each of which involves the minimum disturbance of the existing molecular structure (Hinshelwood 1947). There are, however, some important observations which, though susceptible of treatment by the same general principles, require a more detailed approach. The fact that steam and carbon dioxide react predominantly with different parts of the charcoal surface is the most outstanding. Moreover, the retarding effects of the products have been shown to be caused by chemical adsorption, but their variation from one reaction to another clearly depends on the specific properties of each set of sites. It will be recalled that the action of steam is retarded only by hydrogen, while that of carbon dioxide is retarded by both carbon monoxide and hydrogen. The proposed mechanism indicates that steam and hydrogen should compete for the sites which can take up hydrogen atoms. An analogous explanation

The nature of the active sites

The mechanism deduced for the steam reaction may be expressed in terms of carbon atoms which are attached to the rest of the lattice by only three bonds, and thus have one further orbital available for interaction with other molecules:



† The following bond strengths (heat contents at 25° C) are used throughout this discussion: H—H 104 kcal. (Herzberg 1939); C—H 106 kcal. for trigonal hybridization (Walsh 1947) and 104 kcal. for the tetrahedral state (Long & Norrish 1946); C—O 86 kcal., C=O 184 kcal. (Walsh 1947); C—C 95 kcal. (Long & Norrish 1946), C=C 153 kcal. (Walsh 1946). The dissociation energy of the carbon monoxide molecule into atoms in ³P states is taken to be 211 kcal. (Herzberg 1939), so the bond strength with respect to ³S carbon, the reference state for the other carbon bonds, becomes 277 kcal. (Long & Norrish 1946). Other data required are the heat content changes for the reactions H₂O = OH + H and CO₂ = CO + O; these are found from the information collected by Lewis & von Elbe (1935) to be 116 and 127 kcal. respectively. Although some of these values may be subject to future revision, it is most unlikely that the general conclusions will be seriously affected.

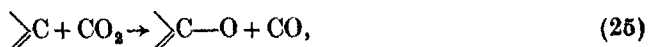
experimental figure of 50 kcal. (Barrer 1935), but it is only to be expected that, since the vacant sites are of the nature of free radicals, they will be stabilized in some degree by resonance. Although the precise canonical states cannot easily be specified, a resonance energy equal to the discrepancy of 29 kcal. per active carbon atom is not improbable. The evolution of gaseous hydrogen from adsorbed steam, which is thought to involve the intermediate transfer of the second hydrogen atom to the carbon surface, has been represented by a single stage in equation (23) merely for convenience of illustration. The bond to the oxygen atom then remaining will clearly have some tendency to become a double one at the expense of a corresponding reduction in the order of a carbon-carbon link. A net increase of 40 kcal. in the strength of the individual bonds would so be obtained, but against that must be set the lack of resonance energy in the resulting quinonoid form, since even a single benzene ring is stabilized by 36 kcal. (Kistiakowsky, Ruhoff, Smith & Vaughan 1936). It is thus a fair approximation for energetic purposes to regard this type of carbon atom as capable of forming only a single bond with any adsorbed atom or group. Radicals with a structure similar to that suggested for the adsorbed oxygen atom have long been known to exist in solution (for a summary, see Waters 1946). The driving force for the final stage of the reaction comes from the formation of the particularly strong bond in the molecule of carbon monoxide which is evolved.

The fact that the sites which react with steam do not adsorb carbon monoxide can also be accounted for by the present treatment. Even if the vacant site was not stabilized in any way, the process



which appears to represent the most favourable possibility, would lead to the evolution of only 2 kcal. As a gas is appreciably adsorbed at high temperatures only if the change is strongly exothermic, it follows that the adsorption of carbon monoxide should be negligible compared with that of steam (76 kcal.) or hydrogen (108 kcal.).

If the initial step in the carbon dioxide reaction is formulated in terms of the sites discussed above, it becomes



which is no less than 117 kcal. more endothermic than the corresponding stage of the steam reaction. According to the concept of chemical inertia (Evans & Polanyi 1938), a difference of this magnitude should lead to a greatly increased activation energy, so it is most unlikely that the process represented by equation (25) would occur at any appreciable rate. In addition to these sites, however, the charcoal surface probably contains a smaller number of atoms which are each able to form two extra bonds; such atoms will be a feature of incomplete benzene rings, and might also exist at special positions on lattice edges which have not yet been attacked. Although they are clearly capable of decomposing the steam molecule, these divalent carbon atoms are no better suited to that purpose than are the other active sites, because neither the hydrogen atom nor the hydroxyl radical can utilize more than

one free valency. No alteration need therefore be made to the treatment of the steam reaction, since the single bond sites may be supposed to make the predominant contribution by virtue of their greater abundance. The distinctive feature of the divalent carbon atoms is the possibility of a double bond, the formation of which will undoubtedly facilitate the disruption of the carbon dioxide molecule:



As this process is estimated to be 83 kcal.‡ more exothermic than that of equation (25), it should require a very much smaller activation energy owing to the increased driving force available (Evans & Polanyi 1938); it is thus thought to be the one responsible for the first stage of the carbon dioxide reaction. This view not only explains the comparative scarcity of the carbon dioxide sites, but will also account for their capacity to take up both carbon monoxide and hydrogen. Carbon monoxide can be adsorbed by the formation of a double bond,



the calculated heat of adsorption of 45 kcal. being in good agreement with the experimental value of 46 kcal. The alternative possibility of two single bonds enables hydrogen to be strongly adsorbed with the evolution of 89 kcal.:



The present scheme is also consistent with the suggestion, made to account for the observed rates of reaction, that the final stage of the mechanism may be non-adiabatic. An electronic transition seems to be quite probable, because either type of active carbon atom is tetravalent while carrying an adsorbed oxygen atom, but may be essentially divalent in the carbon monoxide molecule formed (Long & Walsh 1947). As the two kinds of site are thought to be attached to the rest of the lattice by a different number of bonds, it is understandable that the transmission coefficient should not be the same for the steam and carbon dioxide reactions.

It can thus be seen that the above ideas will account for the main features of the reaction mechanism. In view of present knowledge about the mobility of electrons in conjugated systems, the division of the less firmly bound carbon atoms into those which can form either one or two extra bonds cannot be regarded as more than a convenient approximation for a first approach. The surface probably contains a wide variety of different sites capable of forming bonds of an order almost continuously variable from zero to a value possibly exceeding two. Steam should react with all those which can readily provide a bond of order approaching unity, and

‡ Allowance must be made for the energy required to raise the active carbon atom from the divalent to the tetravalent state. This quantity is not known, but is probably similar to the corresponding one for the CH_4 molecule which is thought to be about 15 kcal. (Long & Norrish 1946). The heat content changes involving the divalent carbon atom are thus calculated from the ordinary bond strengths, and a correction of +15 kcal. made to the results so obtained.

carbon dioxide only with the ones capable of forming with similar facility a link of considerably greater order. Further experimental work with different types of carbon is desirable in order to define more precisely the structural requirements for a given kind of site; on the theoretical side, the quantitative treatments of free valency now being developed by Coulson (1946) and by Daudel & Pullman (1946) offer a promising line of inquiry.

Comparison with results obtained at low pressures

The interaction of charcoal with steam at pressures of less than 1 mm. has recently been investigated by Strickland-Constable (1947) who studied the adsorption of the gases by the static method. Results for the course of reaction at 700° C in good agreement with those described in the present paper were obtained, but a somewhat different interpretation was proposed. Steam was thought to be adsorbed without dissociation, and subsequently to react with the carbon to give molecules of hydrogen and carbon monoxide also held to the surface only by physical forces; the slowest of these changes was considered to be the final desorption of carbon monoxide. This mechanism was based on the observation that evaporation of the adsorbed steam is an important factor at 600° C and can be detected even at 700° C. It was argued that since oxygen and nitrous oxide react extremely rapidly with charcoal at these temperatures, any adsorbed oxygen atoms would immediately be converted into gaseous oxides of carbon and therefore could not be recovered as steam.

The greater part of the evidence relating most directly to the steam reaction itself can hardly be reconciled, however, with the point of view adopted by Strickland-Constable. It has been shown conclusively that although the interaction of hydrogen with charcoal is indeed of a physical nature from -195 to 0° C, it exhibits all the characteristics of a chemical change between 350 and 950° C (Barrer & Rideal 1935; Barrer 1935). The activation energy of 75 kcal. now obtained for the adsorption of steam strongly suggests that the molecule is being dissociated. Direct evidence for the corresponding decomposition of the carbon dioxide molecule (activation energy 68 kcal.) is provided by the simultaneous liberation of the carbon monoxide so produced. The slow evolution of carbon monoxide during the steam reaction, a stage requiring an activation energy of 55 kcal., can then be visualized, not as a purely physical process in which no chemical bonds are either broken or formed, but rather as the removal of a carbon atom from the lattice. The value of 46 kcal. found for the heat of adsorption of carbon monoxide also implies the operation of valency forces. Furthermore, the assumption that a significant amount of physical adsorption is even a possibility under these conditions appears to be inconsistent with fundamental principles. Since the adsorption of a gas is accompanied by a marked decrease of entropy, the process is, in general, sufficiently exothermic to take place to an appreciable extent at high temperatures only if chemical bonds are formed. Dispersion and polarization forces acting on small molecules give rise to interaction energies of only a few kcal.; they have not, as far as the authors are aware, ever been found to cause strong adsorption in the temperature range 700 to 800° C.

It will now be shown that although steam and carbon dioxide are thought to give rise to adsorbed oxygen atoms, the very much greater rates at which oxygen and nitrous oxide react with carbon can, nevertheless, be explained. Whereas the reactions of carbon dioxide and of steam are endothermic, those of oxygen and of nitrous oxide are exothermic. The heat content changes for the conversion of 1 g. atom of carbon into carbon monoxide (Bichowsky & Rossini 1936) are respectively +41, +31, -27 and -46 kcal.; if carbon dioxide is the primary product of the last two reactions, the corresponding values are -94 and -134 kcal. In the exothermic process, as in the endothermic one, oxygen must first be transferred to the carbon surface and must then evaporate as a gaseous oxide of carbon. If carbon monoxide is produced, the second stage must be the same as that of the endothermic mechanism, and even if carbon dioxide is formed, considerable energy will still be required to remove the carbon atom from the lattice. It follows, therefore, that the heat of the exothermic reaction is liberated in the first stage, and consequently that each oxygen atom so adsorbed must possess at first an exceptionally large vibrational energy. After a small number of oscillations, this energy will have been distributed among the many degrees of freedom of the solid; the oxygen atom will then be in the same state as one obtained from carbon dioxide or steam, and will react further only at the comparatively slow speed characteristic of the endothermic oxidation. There is clearly a possibility, however, that before the excess energy is dissipated, it might be used to overcome the large activation energy required to disrupt the carbon lattice. Complete reaction would then take place in an effectively instantaneous process, the speed of which would be limited only by that of the initial adsorption. The latter should be very much faster in the exothermic than in the endothermic reactions, since the activation energy should be considerably reduced by the greatly increased driving force available. It is suggested, therefore, that a process of this type competes with the formation of the relatively stable oxide film, and is responsible for the high speed of the exothermic oxidation.

These considerations not only meet the difficulty raised by Strickland-Constable, but also predict the type of mechanism which is found experimentally. A single stage reaction caused by impact on the clean surface and the simultaneous formation of a retarding film have been observed in many investigations of the oxygen-carbon system (for a summary, see Strickland-Constable 1940); they are illustrated with particular clarity in the work on diamond at 300° C carried out by Barrer (1936*b*). No explanation of why the kinetic behaviour should be of this form appears to have been given hitherto. Nitrous oxide reacts with charcoal at 400° C to form two distinct kinds of surface oxide; a stable compound similar to that produced by oxygen, and a labile compound which with a further molecule of nitrous oxide rapidly evolves carbon dioxide (Strickland-Constable 1938*a, b*). The stable oxide was identified with chemically adsorbed oxygen, but no clear picture of the labile oxide could be offered. The exceptional properties of the latter compound can, however, readily be accounted for if it is regarded as an adsorbed oxygen atom which has not yet lost the excess energy liberated during its formation.

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The control of the temperature of endothermic reactions in flow systems

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The type of flow system which is convenient for investigating the kinetics of many chemical reactions presents special difficulties of temperature control which become increasingly acute the greater the speed of the reaction. If the change is highly endothermic the problem of maintaining a distribution of temperature uniform in space as well as in time becomes of great importance, and unless special precautions are taken the spatial distribution may vary considerably with changes in the rate of reaction. An apparatus is described, utilizing two relay circuits operated by suitably spaced thermocouples, by which the desired automatic regulation of temperature can be achieved.

INTRODUCTION

An account is given below of the special method of temperature control used in the kinetic investigations described in the two preceding papers. The reactions of carbon with carbon dioxide and with steam are both highly endothermic (41 and 31 kcal.), and when they were studied in a flow system, complications due to the absorption of heat became acute as the measurements were extended to higher temperatures. The type of electric furnace normally used for kinetic work was found to develop in the reaction zone an extremely uneven distribution of temperature, which depended markedly on the rate of reaction. However, to make measurements sufficiently accurate for the estimation of reliable activation energies for the individual stages of the reactions, it was essential to maintain a temperature uniform throughout the reaction zone to within $\pm 1^\circ \text{C}$ under all conditions. This was an experimental problem on which there were few published data; it is thought that the method by which it has been solved for the present purpose may be of more general application.

THE EXPERIMENTAL SYSTEM

Some further details of the experimental arrangement are relevant to the following discussion. The silica reaction tube, 3.1 cm. in diameter and 55 cm. in length, fitted loosely inside a silica liner of a vertical electric furnace 38 cm. in length. The gas stream was led in at the bottom of the tube and out at the top. The reaction tube was fitted with a central sheath of 4 mm. diameter silica tubing, and the temperature distribution inside this was explored with a thermocouple made from 26 s.w.g. chromel and alumel wires so that it had a small heat capacity and a quick response. An interval of 1 min. between moving the thermocouple and recording the temperature ensured equilibrium. Errors introduced by slow drifts in the temperature

as a whole were minimized by taking two sets of readings obtained by moving the thermocouple first in one direction and then in the other. The furnace was wound in the way described by Norrish & Wallace (1934) on an externally grooved silica former of pitch ten turns to the inch, using 22 s.w.g. 'Red Fox 135' resistance wire. Tappings were made at four points in the winding, so that five sections of lengths 4.3, 4.3, 14.0, 4.3 and 4.3 cm. were formed. With the reaction tube empty the power dissipation in the various sections was adjusted until a fairly even temperature distribution in the central zone was obtained; this is shown as curve (a) in figure 1.

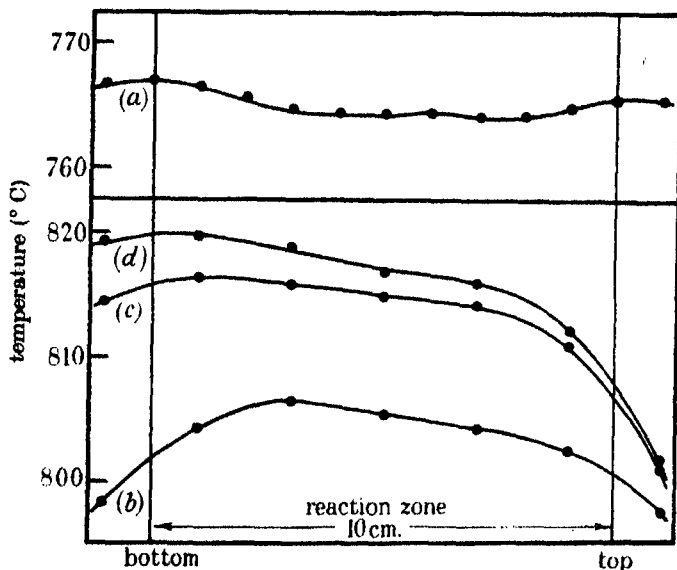


FIGURE 1. Temperature distribution in furnace. Tube packed with silica chips; (a) no gas passing; (b), (c) and (d) air at 1200, 800 and 200 c.c./min.

The temperature of the furnace as a whole was controlled by a second chromel-alumel thermocouple, the e.m.f. of which was balanced by a potentiometer with a mirror galvanometer as a null instrument. When the temperature fell below the desired value, the light reflected from the galvanometer illuminated a photocell operating a relay circuit which increased the furnace current. With a Cambridge 10Ω d'Arsonval galvanometer, regulation in the empty reaction tube to $\pm 0.01^\circ\text{C}$ at 800°C could be obtained. The attainment of this degree of regulation is attributed to the absence of any opaque insulating material, such as alundum or asbestos, to prevent direct radiation from the furnace winding to the controlling thermocouple in the centre of the reaction tube. With the reaction tube empty the time elapsing between a small change in the heating current of the furnace and the response of the control circuit was of the order of 1 or 2 sec.; when the reaction tube contained carbon, or any opaque material, the time lag was about 1 min. and the best regulation which could be obtained was of the order of $\pm 0.2^\circ\text{C}$.

INVESTIGATION OF THE TEMPERATURE DISTRIBUTION

To study the effect of gas flow, the reaction tube was filled with broken silica, and a current of 1200 c.c./min. of air passed through it. After readjustment of the furnace, the fairly even distribution shown as curve (b) in figure 1 was obtained.

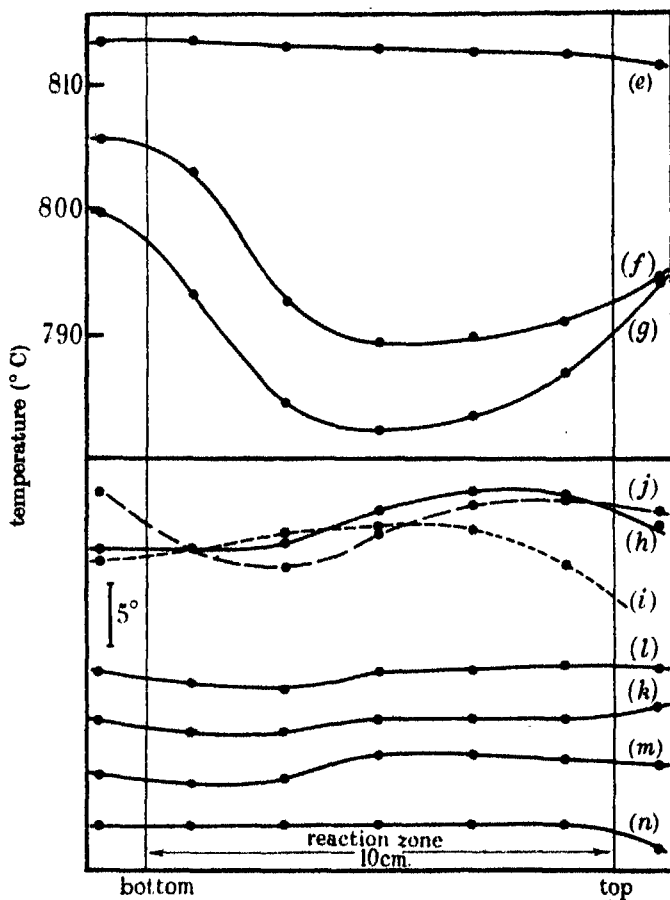


FIGURE 2. Effect of heat of reaction on temperature distribution and its correction. Total rate of flow 1200 c.c./min. (e), (f) and (g) no CO_2 , 129 mm. CO_2 and 380 mm. CO_2 at a given furnace setting. (h), (i) and (j) 380, 129 and 760 mm. CO_2 at another furnace setting. (k), (l), (m) and (n) automatic control at 507, 380 and 253 mm. CO_2 at 755° C, and 253 mm. CO_2 at 775° C.

The distributions (c) and (d) were then obtained by reducing the air current to 600 and 200 c.c./min. without altering the setting of the furnace. In these experiments the temperature as a whole was not controlled, the furnace merely being allowed to attain thermal equilibrium at each of the three rates of flow which were used. It may be seen that the change in the rate of flow did not affect the temperature in the upper part of the furnace, and that in the central zone, although the tem-

perature as a whole rose as the rate of flow was reduced, the form of the distribution was not much changed. These results suggested that the gas stream probably attained the furnace temperature before it reached the central zone, and that small changes of flow and specific heat were not likely, therefore, to be a serious problem in the establishment of a uniform temperature distribution.

The effect of the heat of reaction was investigated as follows. 29.7 g. of charcoal granules were placed between small pads of asbestos fibre in the middle 10 cm. of the reaction tube, and the furnace adjusted to give an even distribution at about 810° C with a rate of flow of 1200 c.c./min. of nitrogen (curve (e), figure 2). Then, keeping the total rate of flow constant, the nitrogen was replaced by various mixtures of carbon dioxide and nitrogen and the temperature distribution redetermined. The distributions (f) and (g), obtained with mixtures containing carbon dioxide at partial pressures of 129 and 380 mm. respectively, show that the heat of reaction, although small compared with the power supplied to the furnace (4 and 6 W respectively compared with 180 W), nevertheless had a very considerable effect on the temperature distribution. Knowing the temperature coefficient of the reaction rate (approx. 2.5 % per °C) and assuming the lower end of the reaction zone to have been maintained at a constant temperature, it was calculated that the observed rates of reaction were only about 70 % of the values which would have been obtained if a uniform temperature had been maintained. An apparatus in which large errors may arise because the temperature of the reaction zone depends on the rate of reaction is obviously unsuitable for kinetic work; these experiments showed clearly that in a flow system of this kind the control of the temperature at a single point is not adequate to ensure uniform conditions of temperature, even if the furnace is adjusted initially to give a suitable temperature distribution.

AUTOMATIC CONTROL OF THE TEMPERATURE DISTRIBUTION

The automatic control of the temperature distribution is made possible by the change in the form of the distribution as the net rate of supply of heat to the reaction zone is varied. This may be seen from the curves (h), (i) and (j) in figure 2. The first of these was obtained by adjusting the furnace to give a fairly even distribution with a gas stream containing carbon dioxide at a partial pressure of 380 mm.; the distributions (i) and (j) were obtained with carbon dioxide pressures of 129 and 760 mm., giving lower and higher rates of reaction respectively. A comparison of these curves shows that in the lower part of the reaction zone the distribution became more concave in form as the rate of reaction was increased. If the furnace had been ideally adjusted so that the distribution for 380 mm. of carbon dioxide had been uniform, then the curve at the lower rate would have been convex in shape and that at the higher rate concave. Now it was known that a convex distribution could be straightened by decreasing the current through the centre section of the furnace winding and a concave one by increasing the current. A differential thermocouple was therefore used to detect the form of the distribution, and to control it by regulating

with an additional relay circuit the power supplied to the centre section of the furnace winding.

The arrangement finally adopted is illustrated in figure 3. The composite thermocouple T consisted of a single 26 s.w.g. chromel wire with alumel wires of the same gauge welded to it. Except at the junctions the wires were carried in narrow, multiple-bore silica tubing, and the whole thermocouple was placed in the central sheath of the reaction tube with its lowest junction at the bottom of the reaction zone. This junction, with the potentiometer P , mirror galvanometer G_2 and relay 2

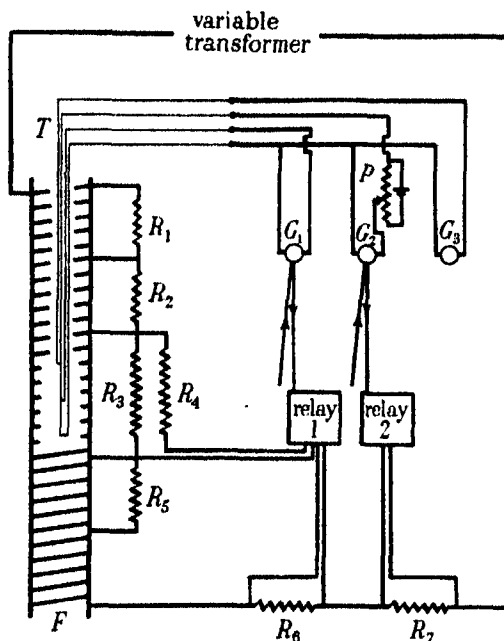


FIGURE 3. Circuit for automatic control of temperature distribution.

shorting the variable resistance R_7 in series with the furnace windings F , controlled the temperature at the bottom of the reaction zone. The e.m.f. between the two lower alumel leads, indicating the nature of the distribution, was applied to the mirror galvanometer G_1 associated with relay 1; the latter placed an additional resistance R_4 in parallel with the centre section of the furnace winding when the distribution became convex. R_4 was chosen so that the operation of the regulator caused a change of about 20 % in the power supplied to the centre section of the furnace winding. Any tendency for the distribution to fluctuate unsymmetrically could easily be seen from the movement of G_1 and corrected by a small adjustment of R_3 , the main resistance across the middle section. A form of coupling between the two control circuits was caused by the drop in the effective resistance of the furnace when R_4 was in circuit. This was eliminated by introducing a compensating resistance R_6 in series with the furnace; R_4 and R_6 were brought into circuit together by relay 1

and R_6 was adjusted so that the total resistance remained constant. To minimize interaction in the thermocouple itself, the leads, and particularly the alumel one which is common to both circuits, should have a low resistance. The 26 s.w.g. wires constituting the thermocouple were therefore joined as near the furnace as possible to heavier leads of the same materials, and these in turn were soldered to 18 s.w.g. copper wire, the copper-chromel and copper-alumel junctions being kept at 0°C . The third junction was added to the thermocouple to indicate on the galvanometer G_3 the difference in temperature between the top and bottom of the reaction zone; this difference could be kept small by an occasional adjustment of R_1 and R_2 . The junctions operating the control circuits were placed at the lower end of the reaction zone, since the rates of reaction were greatest in that region on account of the retarding action of the products formed as the gas stream passed upwards through the charcoal column.

The use of the two control circuits in this way was found to be satisfactory; the temperature distribution was generally uniform to within 2°C and after careful adjustment the variation at any point was of the order of $\pm 0.5^\circ\text{C}$. Some typical records of the temperature distribution during the measurements of the rate of the carbon dioxide reaction at a series of pressures and temperatures are shown in figure 2, curves (k), (l), (m) and (n); they may be compared with the distributions above obtained without the differential control. For the steam reaction, the behaviour of the galvanometers indicated that the thermal conditions were equally satisfactory.

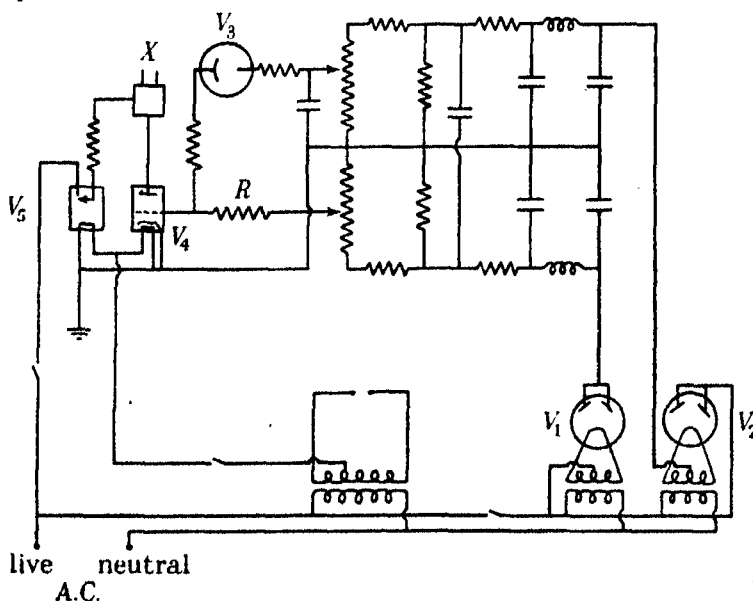


FIGURE 4. Photocell-operated relay circuit. V_1 , V_3 rectifying valves; V_2 caesium gas-filled photocell; V_4 thyatron; V_5 thermal delay switch. X relay. R a resistance comparable with that of the photocell when illuminated.

THE PHOTOCELL-OPERATED RELAY CIRCUIT

The circuit diagram of the photocell operated relay circuit is shown in figure 4. A thyatron valve V_4 fed with an alternating anode voltage is used as a relay, controlled by a photocell V_3 in the grid circuit. The photocell is incorporated in a potentiometer network which is supplied with direct current from an auxiliary rectifying system (V_1 , V_2). When the photocell is in the dark, its resistance is large compared with that of R and the grid of the thyatron is held sufficiently negative for the valve to pass no current. On illuminating the photocell, its resistance falls and the consequent decrease of the negative grid bias allows the thyatron to operate the relay X . This circuit is in some ways more cumbersome than the phase-shift circuits which are commonly used, but it has proved simple in construction and adjustment, and reliable in operation.

The authors are grateful to Professor C. N. Hinshelwood, F.R.S., for his interest and encouragement. This work forms part of the programme of the Fuel Research Board of the Department of Scientific and Industrial Research, and this paper is published by permission of the Department. One of the authors (J.G.) was a member of the Department's staff. The illustrations are Crown copyright and are published by permission of the Controller of His Majesty's Stationery Office.

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The use of interlacing nets for the application of relaxation methods to problems involving two dependent variables

By D. C. GILLES

With a foreword by W. G. BICKLEY

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In the solution, by relaxation methods, of partial differential equations involving more than one dependent variable, it has been customary to find the values of all such variables at the nodes of one net. By considering the relative accuracy of the finite difference approximations to the individual terms of the equations, and for other reasons, it is suggested that values of some of the variables be determined at the centres of the meshes, which amounts to using two interlacing nets. This idea is developed, and the method is applied to a variety of problems.

FOREWORD

Problems involving more than one dependent variable are common in applied mathematics, and while in general an attempt is made to eliminate all but one of these so as to be able to restrict attention to a single 'unknown', this is not always possible, nor is it always convenient. An instance occurs in two-dimensional elastic problems, where the boundary conditions in terms of the stress function are complicated. In applying relaxation methods, it is simpler to work throughout in terms of the components u , v of the displacement, and the so-called ' u - v technique' was invented (Fox & Southwell 1945) for this purpose.

Denoting Cartesian co-ordinates by x , y , and Poisson's ratio by σ , one of the governing equations is

$$\bullet \quad 2(1-\sigma) \frac{\partial^2 u}{\partial x^2} + (1-2\sigma) \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 v}{\partial x \partial y} = 0. \quad (1)$$

The relaxation technique starts from an approximation to this in terms of finite differences, involving values of the wanted functions u , v , at nodes of a net, usually a square net, say of mesh length a . A critical examination of the method indicated that while the effective mesh length used for $\partial^2 u / \partial x^2$ and $\partial^2 u / \partial y^2$ was a , that used for $\partial^2 v / \partial x \partial y$ was really $2a$.

To see this, note first that, using suffixes as indicated in figure 1 to denote the location of the point at which a value of u or v is taken,

$$\frac{u_1 - u_0}{a} \text{ is an approximation to } \frac{\partial u}{\partial x}$$

centred at the mid-point of the segment 01, and so

$$\frac{1}{a} \left(\frac{u_1 - u_0}{a} - \frac{u_0 - u_2}{a} \right) \text{ is an approximation to } \frac{\partial^2 u}{\partial x^2}$$

centred at 0, and using consistently the mesh length a . But, with values of v given at the same mesh points, the best we can do for a finite difference approximation to $\partial^2 v / \partial x \partial y$ is

$$\frac{1}{2a} \left(\frac{v_6 - v_8}{2a} - \frac{v_6 - v_7}{2a} \right),$$

where the first term represents the finite difference approximation to $\partial v / \partial y$ centred at the point 1, and where the fact that the effective mesh length is $2a$ is abundantly evident.

If we wish the mesh length associated with v to be a , so that the accuracy of the v -term in equation (1) may be comparable with that of the other terms, then we must use values of v at the centres of the squares of the net of figure 1, i.e. we must use a

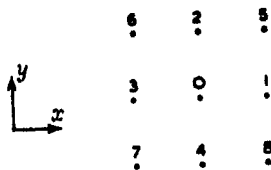


FIGURE 1

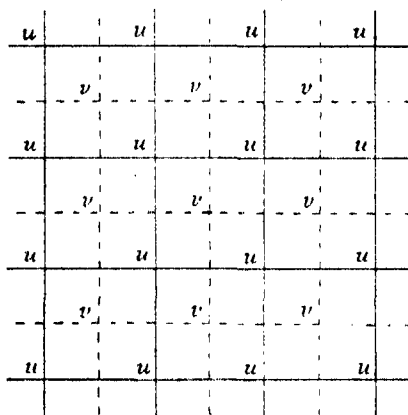


FIGURE 2. The interlacing nets.

separate net for v , which interlaces that for u , as indicated in figure 2. We note immediately that the u -points are at the centres of the squares of the v -net; the relation between the nets is reciprocal, and consequently the finite difference approximation to the other governing equation,

$$(1 - 2\sigma) \frac{\partial^2 v}{\partial x^2} + 2(1 - \sigma) \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 u}{\partial x \partial y} = 0, \quad (2)$$

can be expressed, consistently as to mesh length a , in terms of values at the nodes of the same two interlacing nets.

These ideas were reinforced—coincidentally—by papers by Kron (1944) and Carter (1944) in which an electric circuit analogy, and a network analyzer, were applied to problems in elasticity. In these, u and v are given by potentials at nodes of an electrical network, and it is clearly necessary that u and v be measured at different points, i.e. that two networks (appropriately coupled or interconnected, of course) be used.

Once the idea of interlacing nets is accepted, it becomes clear that there are many other problems involving two unknowns to which they can appropriately be applied

The most obvious disadvantage, that the two unknowns are not determined at the same points, is comparatively trivial compared with the two main advantages, the first (minor) that the use of interlacing nets enables the 'coupling' effects to be more accurately taken into account, and the second (major) that one is dealing with differential equations of lower order than if one variable is first eliminated between the governing equations. For instance, the equations (1) and (2) are each of the second order, whereas the corresponding equation for the stress function is of the fourth order; the finite difference approximation to this equation is more complicated, and also extends over a region of the x - y plane four times as large. In what is probably the simplest instance of the use of interlacing nets, the Laplace equation (second order) is replaced by the Cauchy-Riemann equations, and *both* the conjugate functions are *concurrently* determined.

The ensuing sections illustrate the use of interlacing nets in the solution of a representative variety of problems by relaxation methods. The actual problems are:

- (i) Plane strain with boundary displacements given (§§ 1 to 4).
- (ii) Stresses in a solid of revolution (§§ 5 to 8).
- (iii) The conjugate plane-harmonic functions (§§ 9 to 12).
- (iv) The quasi-plane-harmonic equation (§§ 13 and 14).

The order in which they are given is that in which they were attacked, rather than that of their mathematical content or complexity. W.G.B.

PLANE STRAIN

1. If u and v are the displacements in the x and y directions respectively, then for the two-dimensional elastic problem, the equations of equilibrium may be written as

$$\left. \begin{aligned} 2(1-\sigma) \frac{\partial^2 u}{\partial x^2} + (1-2\sigma) \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 v}{\partial x \partial y} &= 0, \\ (1-2\sigma) \frac{\partial^2 v}{\partial x^2} + 2(1-\sigma) \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 u}{\partial x \partial y} &= 0, \end{aligned} \right\} \quad (3)$$

where σ is Poisson's ratio (Love 1927, § 94).

Using interlacing nets of mesh length a as indicated in the introduction, a typical u -point may be considered, denoted by 0, its four surrounding points 1, 2, 3, 4 and the v -points v, vi, vii, viii. Thus finite difference approximations to the terms in the first of the equations (3) are given as expressions involving the values of u and v at these 9 points by

$$\begin{aligned} \left(\frac{\partial^2 u}{\partial x^2} \right)_0 &= \frac{1}{a} \left(\frac{u_1 - u_0}{a} - \frac{u_0 - u_3}{a} \right) = \frac{1}{a^2} (u_1 + u_3 - 2u_0), \\ \left(\frac{\partial^2 u}{\partial y^2} \right)_0 &= \frac{1}{a} \left(\frac{u_2 - u_0}{a} - \frac{u_0 - u_4}{a} \right) = \frac{1}{a^2} (u_2 + u_4 - 2u_0), \\ \left(\frac{\partial^2 v}{\partial x \partial y} \right)_0 &= \frac{1}{a} \left(\frac{v_v - v_{viii}}{a} - \frac{v_{vi} - v_{vii}}{a} \right) = \frac{1}{a^2} (v_v - v_{vi} + v_{vii} - v_{viii}) \end{aligned}$$

with an error in each case of order a^2 .

Hence the equation may be replaced by its finite difference equivalent, viz.

$$2(1-\sigma)(u_1 + u_3 - 2u_0) + (1-2\sigma)(u_2 + u_4 - 2u_0) + v_v - v_{v1} + v_{v11} - v_{v111} = 0,$$

or in the 'residual' form,

$$(F_u)_0 \equiv 2(1-\sigma)(u_1 + u_3) + (1-2\sigma)(u_2 + u_4) - 2(3-4\sigma)u_0 + v_v - v_{v1} + v_{v11} - v_{v111} = 0. \quad (4)$$

Because of the reciprocal relation between the nets, any typical v -point may be denoted by 0 and the surrounding points lettered as in the diagram (figure 3) whence the second of the equations (3) above may be written as

$$(F_v)_0 \equiv (1-2\sigma)(v_1 + v_3) + 2(1-\sigma)(v_2 + v_4) - 2(3-4\sigma)v_0 + u_v - u_{v1} + u_{v11} - u_{v111} = 0. \quad (5)$$

The field of work is thus covered with these two interlacing nets, the continuous lines for u and the broken lines for v . At all nodes on the u -net there will be values of u and the u -residuals, calculated from the equation (4) above. Similarly, at all nodes of the v -net, there will be values of v and v -residuals calculated from equation (5).

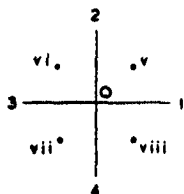


FIGURE 3

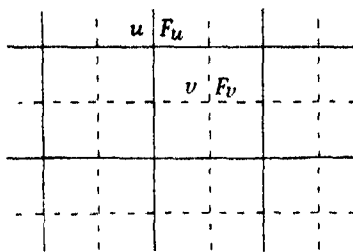


FIGURE 4

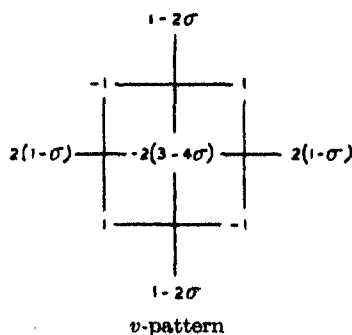
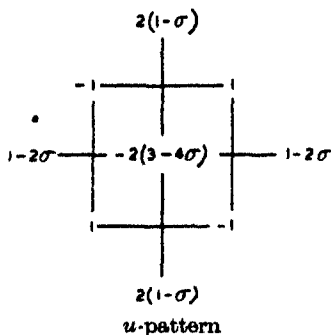


FIGURE 5. The relaxation patterns.

The relaxation process itself is effected with the aid of two 'relaxation patterns', shown in the diagram (figure 5). These are patterns giving the effect on the residuals in the region of the point of adding a unit increment to the value of u or v at that point. Similar patterns have been discussed in other papers on the subject, and interlacing nets introduce here no other new feature as regards their use.

2. It is obvious, however, that the boundary conditions must require some special consideration. If the boundaries are rectangular, the nodes of both nets can be made to lie on the boundaries by taking the mesh lines at 45° to the boundary lines (figure 6).

Then, the values of both u and v on the boundaries being known, the residuals may be calculated for both u and v all over the region.

In all other types of boundary, and for the rectangular case where the boundaries are made to coincide with mesh lines, the problem cannot be solved so easily.

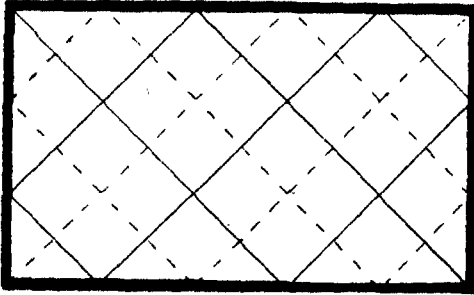


FIGURE 6

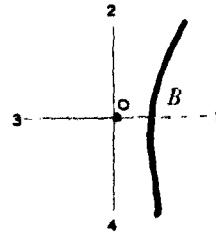


FIGURE 7

Consider a typical u -point lying near to such a boundary, with the mesh lines leading to the point 1 cut by the boundary, so that we have an 'irregular star' (figure 7). The incomplete line O1 may be completed, and led to the point 1 outside the boundary, which is called a 'fictitious' point.

Let $OB = \xi a$, and expand u in the line 301 in powers of x so that

$$u = u_0 + \alpha x + \beta x^2 + \gamma x^3 + \dots$$

Hence, substituting $u_B = u_0 + \alpha \xi a + \beta \xi^2 a^2 + \gamma \xi^3 a^3 + \dots$,

$$u_1 = u_0 + \alpha a + \beta a^2 + \gamma a^3 + \dots,$$

$$u_3 = u_0 - \alpha a + \beta a^2 - \gamma a^3 + \dots$$

Thus $u_1 + u_3 = 2u_0 + 2\beta a^2 + O(a^4)$,

$$u_B + \xi u_3 = (1 + \xi) u_0 + \beta \xi (1 + \xi) a^2 + O(a^3),$$

so, with an error of order a^3

$$a^2 \beta = \frac{u_B + \xi u_3 - (1 + \xi) u_0}{\xi (1 + \xi)},$$

and

$$u_1 = \frac{2}{\xi(1+\xi)} u_B + \frac{1-\xi}{1+\xi} u_3 - \frac{2(1-\xi)}{\xi} u_0. \quad (6)$$

This enables the value of u at the fictitious point 1 to be calculated when the values at the points inside are known. Thus the residuals involving the value of u at this fictitious point can be calculated. For a period of the relaxation the value at this point can be treated as constant, and then when the residuals are checked, it may be adjusted, and then treated as a constant again.

Alternatively this value of u may be introduced into the formulae for the residuals at those points involving the value at the point 1, altering the relaxation patterns at these points. This is usually the best procedure when the boundaries are straight lines and the nodes of one net lie on the boundary.

Similar results hold when any other arm is also a short arm, and also for the value of v at a fictitious point.

3. As an example, consider the extensions of a rectangular steel plate ($\sigma = 0.3$) the sides of which are in the ratio 3 : 1 and boundary displacements are (figure 8)

$$\begin{array}{ll} AB, BC, CD & u = 0, \quad v = 0. \\ AD & u = 0, \quad v = 1000\{4(x/L)^2 - 9\}. \end{array}$$

There is symmetry about the y -axis, where clearly $u = 0$, so that only the right-hand half of the plate will be considered.

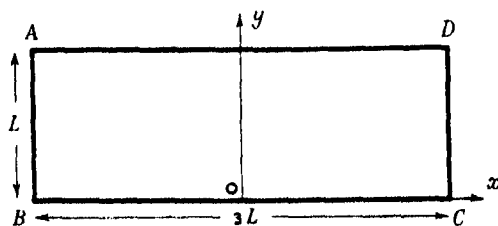


FIGURE 8

Two ways of placing the nets for convenience are open to us, with the mesh lines parallel to, or at 45° with, the sides of the rectangle. We choose the former.

Taking the v -net to lie on the boundary, the u -net therefore straddles it. For these u -points $\xi = \frac{1}{2}$ and $u = 0$ all round, so that the fictitious value is given by

$$u_1 = \frac{2}{3}u_B + \frac{1}{3}u_3 - 2u_0 = \frac{1}{3}u_3 - 2u_0 \quad (u_B = 0),$$

and similarly when u_3, u_4 are fictitious.

The general equations are, since $\sigma = 0.3$,

$$(F_u)_0 \equiv 1.4(u_1 + u_3) + 0.4(u_2 + u_4) - 3.6u_0 + v_v - v_{v1} + v_{v11} - v_{v111} = 0,$$

$$(F_v)_0 \equiv 0.4(v_1 + v_3) + 1.4(v_2 + v_4) - 3.6v_0 + u_v - u_{v1} + u_{v11} - u_{v111} = 0,$$

and for the incomplete stars, the value of u was substituted in the residual formula from the relation above.

In practice the coefficients were multiplied by 15 to make them all integers.

A mesh length, $a = \frac{1}{2}L$, was first considered, and then by trisecting this, a mesh length $a = \frac{1}{6}L$, which had the advantage that all the previous nodes were still nodes of the new nets. From these results, estimates were made for values at the nodes of nets of mesh length $a = \frac{1}{6}L$ and the solution for this net size obtained to compare with that for a net of mesh length $a = \frac{1}{6}L$ but without interlacing nets (Allen & Southwell 1944). These last three results are given (figures 9 to 11).

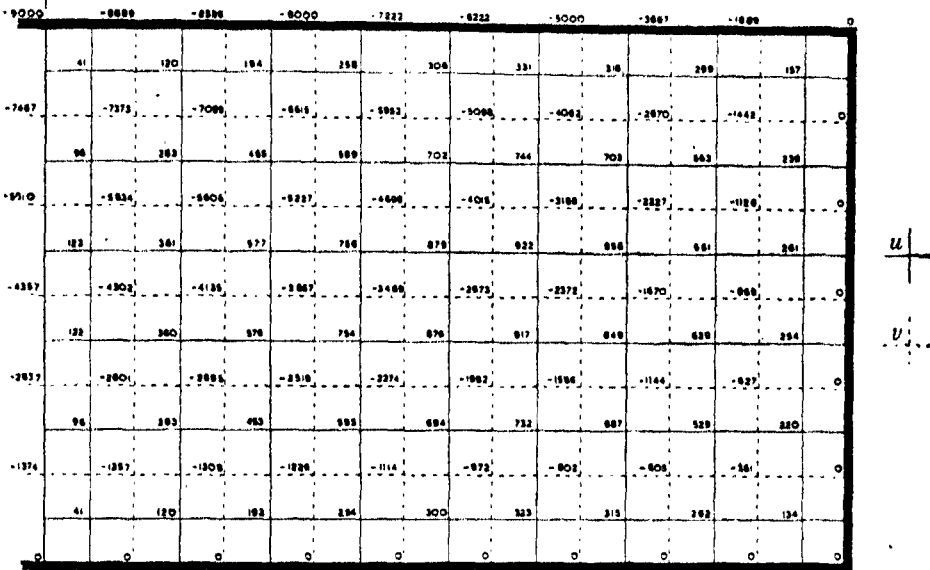


FIGURE 9. Displacements in a plate, mesh length $a = \frac{1}{4}L$.

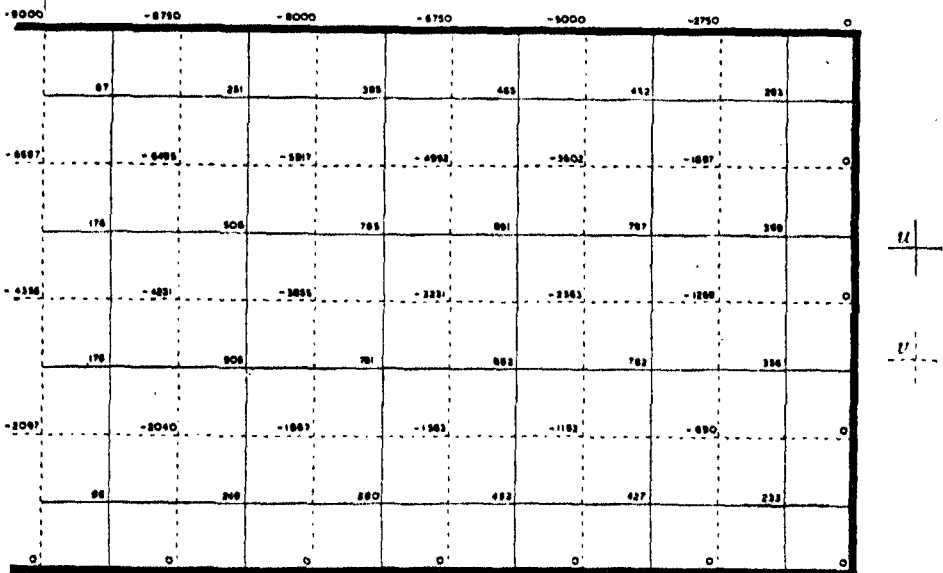


FIGURE 10. Displacements in a plate, mesh length $a = \frac{1}{4}L$.

If the four surrounding points, at which values of u and v are known are labelled i, ii, iii, iv it may be seen that, centred at this point A ,

$$\left(\frac{\partial u}{\partial x}\right)_A = \frac{1}{a}(u_i - u_{iii}), \quad \left(\frac{\partial v}{\partial y}\right)_A = \frac{1}{a}(v_{ii} - v_{iv}),$$

with effective mesh length a , so that the accuracy is not impaired. Hence at an A -point

$$\begin{aligned} \widehat{xx} &= \{(\lambda + 2\mu)(u_i - u_{iii}) + \lambda(v_{ii} - v_{iv})\}/a, \\ \widehat{yy} &= \{\lambda(u_i - u_{iii}) + (\lambda + 2\mu)(v_{ii} - v_{iv})\}/a. \end{aligned} \quad (8)$$

Likewise at a B -point, expressions for $(\partial v/\partial x)$, $(\partial u/\partial y)$ may be obtained, and

$$\widehat{xy} = \mu(v_i - v_{iii} + u_{ii} - u_{iv})/a. \quad (9)$$

Thus the stresses may all be evaluated. They have been computed for the plate problem, using the results for the mesh length $a = \frac{1}{8}L$, and are given in figure 13.

STRESSES IN A SOLID OF REVOLUTION

5. If U and w are the displacements in the r - and z -directions in a stressed solid of revolution, then the dilatation Δ and the rotation ϖ are given by

$$\Delta = \frac{\partial U}{\partial r} + \frac{U}{r} + \frac{\partial w}{\partial z}, \quad 2\varpi_\theta = \frac{\partial U}{\partial z} - \frac{\partial w}{\partial r}, \quad \varpi_r = \varpi_z = 0.$$

Putting $u = rU$, these may be reduced to

$$\Delta = \frac{1}{r} \frac{\partial u}{\partial r} + \frac{\partial w}{\partial z}, \quad 2\varpi_\theta = \frac{1}{r} \frac{\partial u}{\partial z} - \frac{\partial w}{\partial r},$$

and the equations of equilibrium in terms of u and w can then be shown to be

$$\begin{cases} 2(1-\sigma)r \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial u}{\partial r} \right) + (1-2\sigma) \frac{\partial^2 u}{\partial z^2} + r \frac{\partial^2 w}{\partial r \partial z} = 0, \\ (1-2\sigma) \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial w}{\partial r} \right) + 2(1-\sigma) \frac{\partial^2 w}{\partial z^2} + \frac{1}{r} \frac{\partial^2 u}{\partial r \partial z} = 0, \end{cases} \quad (10)$$

where σ is Poisson's ratio (Love 1927, § 99).

Using interlacing nets as before, the continuous lines for u and the broken lines for w , a typical u -point can be denoted by 0, its four surrounding u -points by 1, 2, 3, 4 and the w -points by v, vi, vii, viii. If the mid-points of the arms 01, 02, 03, 04 are lettered i, ii, iii, iv as shown in figure 14, then using a mesh length a

$$a \left(\frac{\partial u}{\partial r} \right)_{ii} = u_2 - u_0 + O(a^3), \quad a \left(\frac{\partial u}{\partial r} \right)_{iv} = u_0 - u_4 + O(a^3),$$

so that

$$\begin{aligned} a^2 \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial u}{\partial r} \right) \right]_0 &= a \left(\frac{1}{r} \frac{\partial u}{\partial r} \right)_{ii} - a \left(\frac{1}{r} \frac{\partial u}{\partial r} \right)_{iv} + O(a^4) \\ &= \frac{1}{r_{ii}} (u_2 - u_0) - \frac{1}{r_{iv}} (u_0 - u_4) + O(a^3). \end{aligned}$$

Thus with an error of order a^3 ,

$$a^2 \left[r \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial u}{\partial r} \right) \right]_0 = \frac{r_0}{r_{11}} (u_2 - u_0) + \frac{r_0}{r_{1v}} (u_4 - u_0),$$

and, as before, to the same order of error,

$$a^2 \left(\frac{\partial^2 u}{\partial z^2} \right)_0 = u_1 + u_3 - 2u_0, \quad a^2 \left(\frac{\partial^2 w}{\partial r \partial z} \right)_0 = w_v - w_{v1} + w_{v11} - w_{v111}.$$

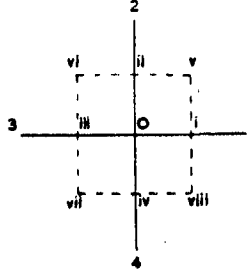


FIGURE 14

Thus the first of equations (10) may be replaced by the finite difference equivalent,

$$\begin{aligned} (F_u)_0 &\equiv 2(1-\sigma) \left\{ \frac{r_0}{r_{11}} (u_2 - u_0) + \frac{r_0}{r_{1v}} (u_4 - u_0) \right\} \\ &+ (1-2\sigma) (u_1 + u_3 - 2u_0) + r_0 (w_v - w_{v1} + w_{v11} - w_{v111}) = 0. \end{aligned} \quad (11)$$

In a like manner, a typical w -point may be denoted by 0, and the surrounding points may be lettered as in figure 14, whence finite difference approximations for the terms in the second of equations (10) may be obtained; in particular, that for the first term is

$$a^2 \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial w}{\partial r} \right) \right]_0 = \frac{r_{11}}{r_0} (w_2 - w_0) + \frac{r_{1v}}{r_0} (w_4 - w_0).$$

Hence the finite difference equivalent of this equation is

$$\begin{aligned} (F_w)_0 &\equiv (1-2\sigma) \left\{ \frac{r_{11}}{r_0} (w_2 - w_0) + \frac{r_{1v}}{r_0} (w_4 - w_0) \right\} \\ &+ 2(1-\sigma) (w_1 + w_3 - 2w_0) + \frac{1}{r_0} (u_v - u_{v1} + u_{v11} - u_{v111}) = 0. \end{aligned} \quad (12)$$

From these equations, the residuals may be calculated and recorded as in the problem of plane strain (§1 and figure 4). The relaxation patterns can be obtained from the equations (11) and (12) but are more complicated, and since they involve values of r , they vary from line to line.

In practice, it was found convenient to bring the coefficients of u_1 , u_3 and w_1 , w_3 to unity by division by the appropriate factor.

6. In this problem also, owing to the nature of the nets, the boundary conditions require special consideration. Even with rectangular boundaries, the nodes of both nets cannot in general here be made to lie on the boundaries since the directions of the axes of r and z (and hence of the nets) are inherent in the form of the equations (10). If any change is made in these directions, the form of the equations is altered, and they become even more complicated.

If the displacements U and w are given on the boundaries, then any 'irregular stars' may be tackled as in the problem of plane strain § 2 using the formula (6) there obtained.

Clearly, however, another type of condition could be imposed, that of known stresses over all or part of the boundaries. It may be shown (Love 1927, § 99) that the stresses are expressed in terms of u and w by the equations

$$\left. \begin{aligned} \widehat{rr} &= 2(\lambda + \mu) \left\{ \frac{\sigma}{r} \frac{\partial u}{\partial r} + (1 - 2\sigma) \frac{\partial}{\partial r} \left(\frac{u}{r} \right) + \sigma \frac{\partial w}{\partial z} \right\}, \\ \widehat{zz} &= 2(\lambda + \mu) \left\{ \frac{\sigma}{r} \frac{\partial u}{\partial r} + (1 - \sigma) \frac{\partial w}{\partial z} \right\}, \\ \widehat{rz} &= \mu \left(\frac{1}{r} \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r} \right). \end{aligned} \right\} \quad (13)$$

If the boundary is a line parallel to the r - or z -axis, then two of these stresses will be known, and the corresponding equations can be used to give the values of u and w along this part of the boundary, and at any fictitious point that may occur.

If the boundary is not such a line, then the stresses may be written in terms of $\widehat{vr}$ and $\widehat{vz}$, where v is the direction of the outward normal. Then, referring to figure 15, these may be taken in terms of the stresses in equations (13) by (Love 1927, § 47).

$$\widehat{vr} = \widehat{rr} \cos(r, v) + \widehat{rz} \sin(r, v), \quad \widehat{vz} = \widehat{zz} \sin(r, v) + \widehat{rz} \cos(r, v). \quad (14)$$

These relations may be used, together with the equations (13) to convert the stress boundary conditions to conditions in u and w .

7. As an example of mixed boundary conditions, the problem taken was that of the displacements in a solid steel cylinder ($\sigma = 0.3$) radius R and length $3R$, subject to the boundary conditions $\widehat{zz} = \widehat{rz} = 0$ over the ends, and $U = 1000R$, $w = 0$ over the surface (figure 16).

Considering a section through the axis it is evident that there is symmetry about the r -axis, where $w = 0$ and hence only one-half of the section need be considered. The boundary conditions along AB suggest that the u -net should be taken to lie on this line so that the values at the fictitious points for w are given by

$$w_3 = \frac{8}{3}w_B + \frac{1}{3}w_4 - 2w_0 = \frac{1}{3}w_4 - 2w_0,$$

since $\xi = \frac{1}{2}$ and $w_B = 0$.

On the boundary BC , the stress conditions give, from equations (13)

$$\widehat{z}\widehat{z} = 2(\lambda + \mu) \left\{ \frac{\sigma}{r} \frac{\partial u}{\partial r} + (1 - \sigma) \frac{\partial w}{\partial z} \right\} = 0, \quad \widehat{z}\widehat{r} = \mu \left(\frac{1}{r} \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r} \right) = 0. \quad (15)$$

From the first of these equations

$$\sigma \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial u}{\partial r} \right) + (1 - \sigma) \frac{\partial^2 w}{\partial r \partial z} = 0 \quad (16)$$

is obtained. Let the u -net lie on the boundary BC . Then a typical portion of this boundary is shown in figure 17 with the 'fictitious' u - and w -points introduced.

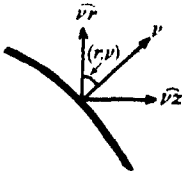


FIGURE 15

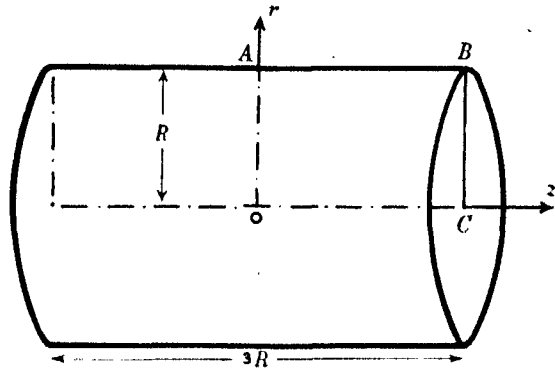


FIGURE 16

Considering a typical u -point lying on the boundary, and lettering the points in the normal manner, the finite difference approximations to the second of equations (15) and to equation (16) can be shown to be, centred at this point 0,

$$u_1 - u_3 + r_0(w_v + w_{v1} - w_{v11} - w_{v111}) = 0,$$

$$\frac{\sigma}{r_{11}}(u_2 - u_0) - \frac{\sigma}{r_{1v}}(u_0 - u_4) + (1 - \sigma)(w_v - w_{v1} + w_{v11} - w_{v111}) = 0.$$

Hence, in the equation for the residual at this point, viz.

$$\begin{aligned} (F_u)_0 &\equiv 2(1 - \sigma) \left\{ \frac{r_0}{r_{11}}(u_2 - u_0) + \frac{r_0}{r_{1v}}(u_4 - u_0) \right\} \\ &\quad + (1 - 2\sigma)(u_1 + u_3 - 2u_0) + r_0(w_v - w_{v1} + w_{v11} - w_{v111}) = 0, \end{aligned} \quad (11)$$

the value of u for the fictitious point 1 can be substituted, and one obtains

$$\begin{aligned} (F_u)_0 &\equiv 2(1 - \sigma) \left\{ \frac{r_0}{r_{11}}(u_2 - u_0) + \frac{r_0}{r_{1v}}(u_4 - u_0) \right\} + 2(1 - 2\sigma)(u_3 - u_0) \\ &\quad - r_0(1 - 2\sigma)(w_v + w_{v1} - w_{v11} - w_{v111}) + r_0(w_v - w_{v1} + w_{v11} - w_{v111}) = 0. \end{aligned}$$

At the point B , where the boundary is cut by a w -line, a finite difference approximation to the first of equations (15) may be found, and is, using the lettering indicated in the figure,

$$\frac{\sigma}{r_B} (u_v - u_{vIII}) + (1 - \sigma) (w_1 - w_0) = 0.$$

Since $r_B = r_0$ this may be written as

$$w_1 = w_0 - \frac{\sigma}{r_0(1 - \sigma)} (u_v - u_{vIII}) = w_0 - \frac{3}{7r_0} (u_v - u_{vIII}),$$

enabling the 'fictitious' value w_1 to be found in terms of the values of the functions at points inside the boundary. This may be substituted in the equation (12) for the w -residual involving this fictitious point.

Naturally the relaxation patterns for these points will be altered, and the new patterns can easily be found. It is interesting to note that the patterns for the neighbouring points are not affected in any way.

The general residual formulae (11) and (12) become

$$(F_u)_0 \equiv u_1 + u_3 + \frac{7}{2} \left(\frac{r_0}{r_{11}} u_2 + \frac{r_0}{r_{1v}} u_4 \right) - \left\{ 2 + \frac{7}{2} \left(\frac{r_0}{r_{11}} + \frac{r_0}{r_{1v}} \right) \right\} u_0 + \frac{5r_0}{2} (w_v - w_{v1} + w_{v11} - w_{v111}) = 0,$$

$$(F_w)_0 \equiv w_1 + w_3 + \frac{2}{7} \left(\frac{r_{11}}{r_0} w_2 + \frac{r_{1v}}{r_0} w_4 \right) - \left\{ 2 + \frac{2}{7} \left(\frac{r_{11}}{r_0} + \frac{r_{1v}}{r_0} \right) \right\} w_0 + \frac{5}{7r_0} (u_v - u_{v1} + u_{v11} - u_{v111}) = 0,$$

and those involving other fictitious points were obtained by substituting the values at these points in the general formulae.

A mesh length $a = \frac{1}{2}R$ was first taken, and this followed by taking $a = \frac{1}{3}R$. The relaxation involved no great difficulty, but since the centre increment in the relaxation patterns was about -9 for an increment to u and -2.6 for an increment to w , the values of u were taken to one decimal place to complete the relaxation. This enabled the values of $U = u/r$ to be computed to the nearest integer to compare in accuracy with the w -values. This final solution is given in figure 18.

8. As in all elastic problems it is the stresses themselves that are frequently of greater importance than the displacements, and they may be obtained from the recorded values of the displacements in a manner similar to that in the plane strain problem (§4).

As in this earlier case, there are in addition to the nodes of the continuous line and broken line nets two other kinds of node which have been called A - and B -points, and it is at such points that the stresses can be evaluated.

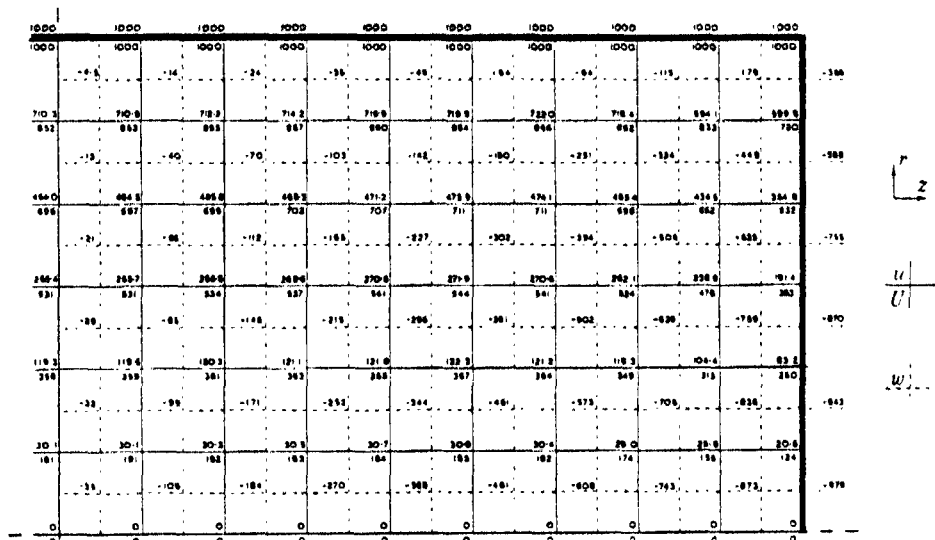
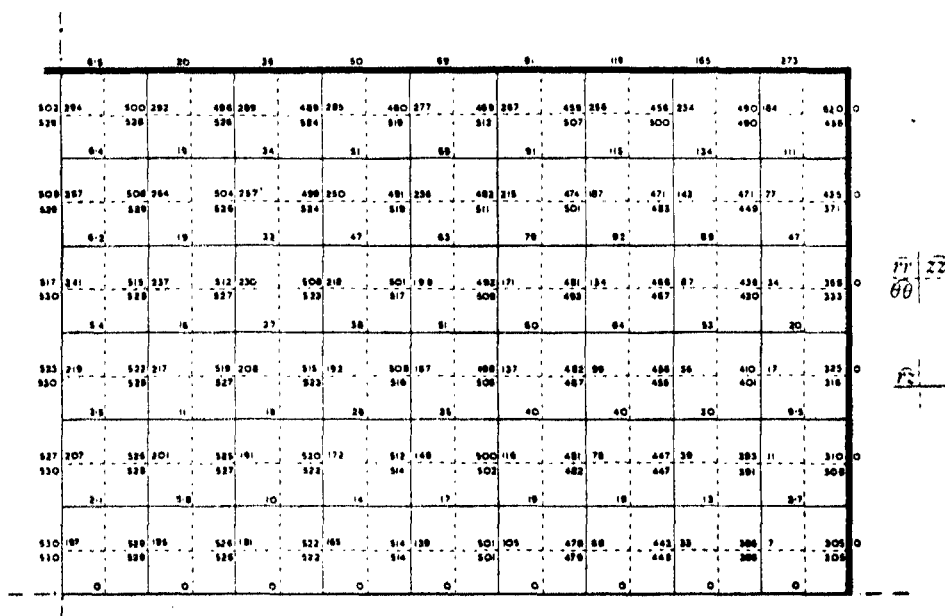
FIGURE 18. Displacements in a cylinder, mesh length $a = \frac{1}{4}R$.

FIGURE 19. Stresses in the cylinder.

[Note. These numbers must be multiplied by 10^6 and the ratio $\frac{U\text{-extension on surface}}{\text{radius of cylinder, } R}$ to give the stresses in lb./sq.in.]

The stresses are expressed in terms of u and w by the equations (Love 1927, § 99)

$$\left. \begin{aligned} \widehat{rr} &= 2(\lambda + \mu) \left\{ \frac{\sigma}{r} \frac{\partial u}{\partial r} + (1 - 2\sigma) \frac{\partial}{\partial r} \left(\frac{u}{r} \right) + \sigma \frac{\partial w}{\partial z} \right\}, \\ \widehat{\theta\theta} &= 2(\lambda + \mu) \left\{ (1 - \sigma) \frac{1}{r} \frac{\partial u}{\partial r} - (1 - 2\sigma) \frac{\partial}{\partial r} \left(\frac{u}{r} \right) + \sigma \frac{\partial w}{\partial z} \right\}, \\ \widehat{zz} &= 2(\lambda + \mu) \left\{ \frac{\sigma}{r} \frac{\partial u}{\partial r} + (1 - \sigma) \frac{\partial w}{\partial z} \right\}, \\ \widehat{zr} &= \mu \left(\frac{1}{r} \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r} \right). \end{aligned} \right\} \quad (17)$$

Considering a B -point (§ 4 and figure 12), the values of w will be known at the points i and iii, and of u and the displacement $U = u/r$ at points ii and iv. Hence the finite difference approximations for the terms in the first three of equations (17) may be deduced at such a point, and are, using a mesh length a ,

$$\left(\frac{\partial w}{\partial z} \right) = \frac{1}{a} (w_i - w_{iii}), \quad \left(\frac{\partial u}{\partial r} \right) = \frac{1}{a} (u_{ii} - u_{iv}), \quad \frac{\partial}{\partial r} \left(\frac{u}{r} \right) = \frac{\partial U}{\partial r} = \frac{1}{a} (U_{ii} - U_{iv}),$$

so that these stresses $\widehat{rr}$, $\widehat{\theta\theta}$, $\widehat{zz}$ may be determined.

Similarly, at an A -point the stress $\widehat{zr}$ can be determined.

The stresses were computed for the solid cylinder problem of § 7 and are given in figure 19.

THE CONJUGATE PLANE-HARMONIC FUNCTIONS

9. The next, and perhaps both the simplest and the most striking, application of interlacing nets is to the determination of conjugate plane-harmonic functions. If ϕ and ψ are such functions then they are connected by the Cauchy-Riemann equations

$$\frac{\partial \phi}{\partial x} = \frac{\partial \psi}{\partial y} \quad \text{and} \quad \frac{\partial \phi}{\partial y} = -\frac{\partial \psi}{\partial x}, \quad (18)$$

and it is to these equations that one looks for the wanted functions.

Using again two interlacing nets, the continuous lines for ϕ and the broken for ψ , consider a portion of the field (figure 20).

In addition to the nodes of the ϕ - and ψ -nets (ϕ - and ψ -points), there are two other kinds of points where a continuous line crosses a broken line. Typical points are again indicated by A and B in the diagram, the points being where a ϕ -line and a ψ -line is in the x -direction respectively.

At the point A , labelling the four surrounding net points, which are ϕ - or ψ -points, by 1, 2, 3, 4, with an effective mesh length a , and centred at the point A ,

$$\frac{\partial \phi}{\partial x} = \frac{1}{a} (\phi_1 - \phi_3), \quad \frac{\partial \psi}{\partial y} = \frac{1}{a} (\psi_2 - \psi_4),$$

so that the first of the Cauchy-Riemann equations (18) becomes

$$\phi_1 - \phi_3 = \psi_2 - \psi_4,$$

or as is better for relaxation purposes

$$F_A \equiv \phi_1 - \phi_3 - \psi_2 + \psi_4 = 0. \quad (19)$$

Considering the point B , in a similar manner it can be seen that the second of the equations (18) may be written as

$$\phi_2 - \phi_4 = -(\psi_1 - \psi_3), \quad \text{or} \quad G_B \equiv \phi_2 - \phi_4 + \psi_1 - \psi_3 = 0. \quad (20)$$

From these two equations the residuals may be calculated in the usual way for the existing values ϕ and ψ , but, and here is the new feature, the residuals are not at the nodes of the ϕ - and ψ -nets but at the A - and B -points. Once this idea is accepted it will be found that there are manifest advantages in this method.

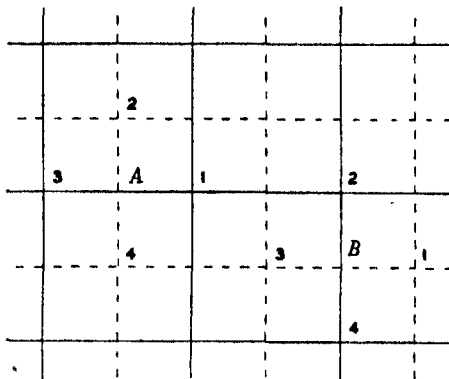


FIGURE 20. The net points.

10. The relaxation patterns, showing the effect on the surrounding residuals for a unit increment to a value of ϕ or ψ are given in figure 21.

It can be seen that each pattern moves residual in a certain direction—that for ϕ diagonally downwards from right to left, and that for ψ diagonally upwards from right to left. This ‘sweep’ of the residual may be used in the relaxation to move a residual as may be required in order most speedily to ‘liquidate’ it. Continual employment of this point-relaxation will eventually reduce the residuals approximately to zero. The relaxation is then complete.

Naturally this process is both laborious and tedious, and clearly it is useful to consider the effect upon the residuals of adding a unit increment to two or more adjacent ϕ - or ψ -values at the same time. Such increments are referred to as blocks, and the process is called block-relaxation. The pattern for a block may be built up by applying the separate patterns for ϕ or ψ at all the points in question. It will then be seen that the pattern for the block preserves the ‘sweeping’ tendency

of the patterns for the individual points, and alters only the residuals at the points immediately outside the boundary of the block. An illustration is given in figure 22, the block consisting of ϕ -points. Clearly the application of such a block will move residuals from one region to another and so eliminate the residuals more quickly than by point-relaxation.

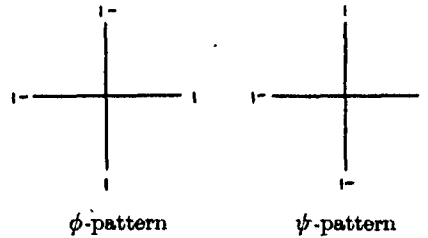


FIGURE 21. The relaxation patterns.

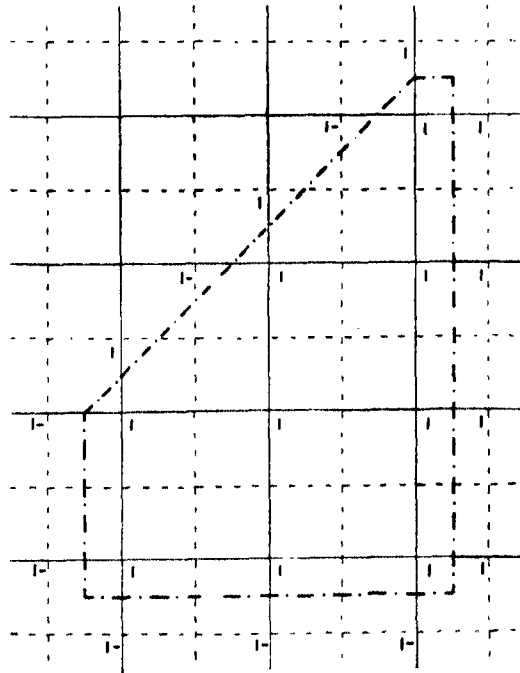


FIGURE 22. Block-relaxation.

11. In conformal transformation, and indeed in all cases where the conjugate functions are required, the values of both functions cannot be specified all round the boundary. Consider as an example the conformal transformation of a circular sector (figure 23), which will be solved later by the relaxation technique (§ 12). If the outer radius of the sector is R , the inner radius 1, and the angle of the sector $\frac{1}{2}\pi$

then conditions can be imposed on the values of ϕ or ψ on three sides of the boundary, but not on the fourth.

With the conditions $\phi = 0$ on BC , $\psi = 0$ on AB and $\psi = 1000$ on DC , the analytic solution can be shown to be, in polar co-ordinates,

$$\phi = \frac{4000}{\pi} \log_e \frac{r}{R} \quad \text{and} \quad \psi = \frac{4000}{\pi} \theta$$

so that the value on the fourth side, the arc AD where $r = 1$, is

$$\phi = -4000(\log_e R)/\pi,$$

and is hence a constant and completely determined. This applies to all such cases involving the two conjugate functions, the values of the functions can be specified on parts of the boundary only, and not all round, i.e. there must be an 'open' part of the boundary where the value of one function is unspecified, but must be constant.

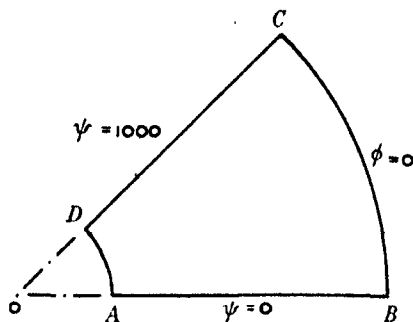


FIGURE 23. Transformation of a sector.

The procedure adopted therefore in the relaxation technique is to lay down values of the functions all over the field, including the 'open' part of the boundary, and calculate the residuals by use of the equations (19) and (20). The relaxation is then effected by elimination of the residuals one with another where possible, and should residuals of one sign predominate, 'sweeping' these residuals towards the 'open' part of the boundary, utilizing the sweeping effect of the relaxation patterns, to which reference has already been made. The unknown constant value of the function on this 'open' part of the boundary is thus altered, and finally attains the correct value.

As an illustration of the method with straight boundaries, the problem of the electric field in a homogeneous isotropic medium of dielectric constant κ between two long conductors of square section has been tackled (figure 24). Because of symmetry, only one-eighth of the field, the section $ABCD$, was considered.

The electric field in a medium is governed by the equations

$$\kappa \frac{\partial V}{\partial x} = \frac{\partial \chi}{\partial y} \quad \text{and} \quad \kappa \frac{\partial V}{\partial y} = -\frac{\partial \chi}{\partial x},$$

where V is the potential and χ a flux function, $\chi = \text{constant}$ giving the lines of electric force.

Since κ is a constant, these equations may be written as

$$\frac{\partial V}{\partial x} = \frac{\partial}{\partial y} \left(\frac{\chi}{\kappa} \right) \quad \text{and} \quad \frac{\partial V}{\partial y} = - \frac{\partial}{\partial x} \left(\frac{\chi}{\kappa} \right)$$

which are formally equivalent to the Cauchy-Riemann equations.

Hence the problem resolves itself to the determination of two conjugate functions, $\phi = V$, and $\psi = \chi/\kappa$, by the method indicated above.

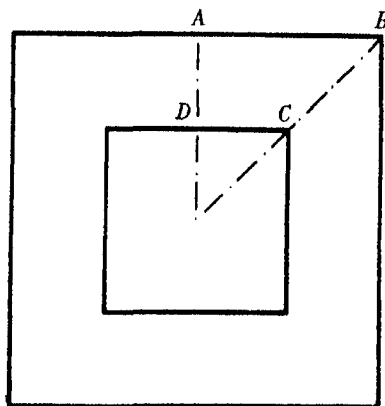


FIGURE 24. Electric field between two square conductors.

The potentials of the inner and outer conductors were taken as 0 and 1000 V respectively, and clearly AD and BC are lines of electric force, hence on these lines ψ is a constant. Since values of ϕ and ψ cannot be specified on all parts of the boundary, the value $\psi = 0$ was taken on BC , and the side AD left 'open'. The squares were considered to have sides in the ratio 9:17, thus enabling AD to be a ψ -line and AB and DC to be ϕ -lines. The problem thus specified presented no difficulty at all, and the solution, values of $\phi = V$ and $\psi = \chi/\kappa$, is given in figure 25.

The above problem with the sides of the square conductors in the ratio 9:17 is rather artificial, a more practical aspect being obtained by taking the sides in the ratio 1:2. An approximate solution to this latter problem has been obtained by Jeffreys (1946), but the problem can easily be solved using the relaxation technique. Referring to figure 24, the side AD on which ψ is a constant, is now a ϕ -line, so that the symmetrical property of the voltages about AD must be used, or, alternatively, the relaxation may be effected on a field twice the size.

The symmetry may be used in the following way. Since the values of ϕ on the adjacent ϕ -lines parallel to AD will be the same, it follows that the differences $\partial\phi/\partial x$, and hence $\partial\psi/\partial y$, will be equal in magnitude but opposite in sign. Introducing a row of fictitious ψ -points, therefore, the differences between these ψ -points must be kept equal in magnitude but opposite in sign to the corresponding differences between the ψ -points on the line just inside the field.

The relaxation can then be effected in the usual manner. This row of fictitious points will form the 'open' boundary, and an increment can be put on all the points to eliminate residuals of one kind or another. Whenever an increment is made to

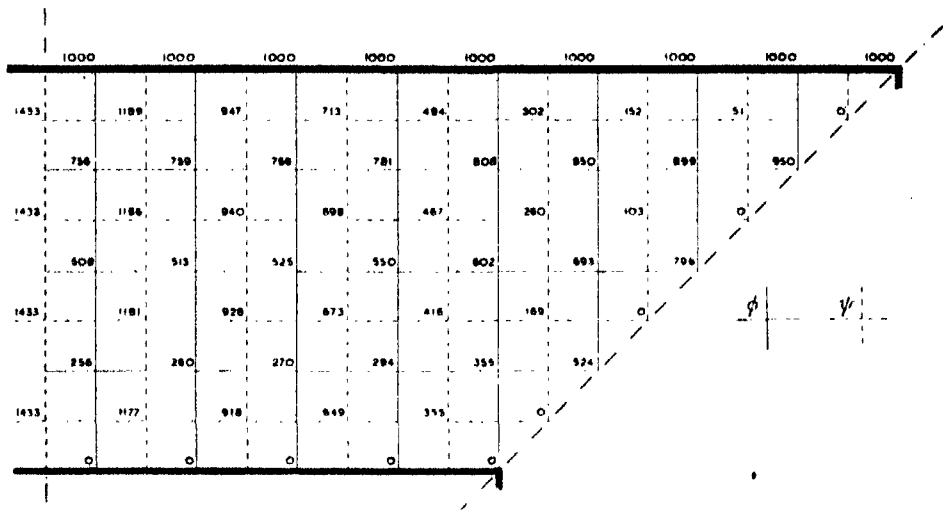


FIGURE 25. Electric field between two square conductors, sides in ratio 9:17.

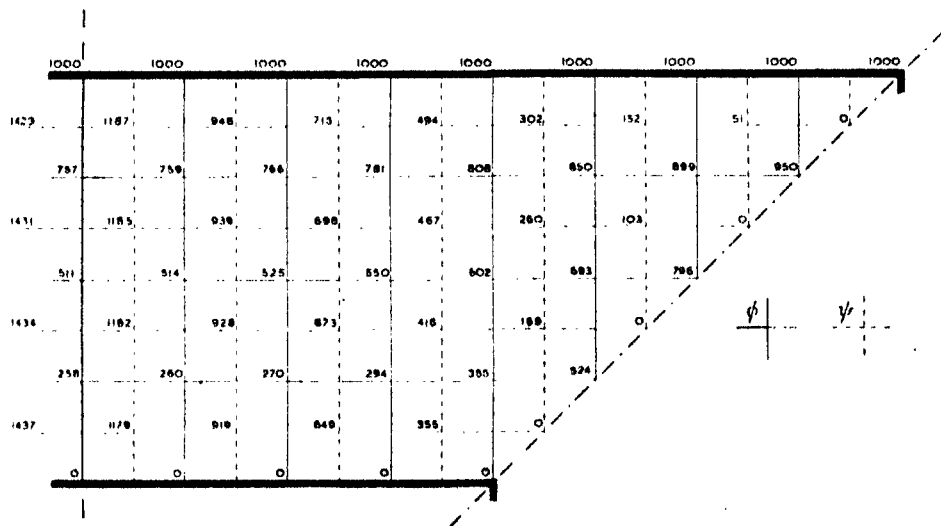


FIGURE 26. Electric field between two square conductors, sides in ratio 1:2.

a ψ -value adjacent to the boundary AD , an equal and opposite one must be made to the corresponding fictitious point. The solution to the problem is given in figure 26.

It is of interest in these two problems to calculate the charge on the inner conductor or the capacitance per unit length. This may be done by considering Gauss's theorem

over any closed curve containing the inner conductor. For obvious reasons the closed curves are here chosen to be squares concentric with the conductors. The integral, $\int (-\partial\phi/\partial n) ds$, may then be evaluated around the four possible squares each bounded by ψ -lines, using a formula for numerical integration, and the average value used to calculate the capacitance. Since the differences are comparatively small, the trapezium rule may be suitably applied. The values for the integrals taken over the section considered in the relaxation for the two problems are given below, that for the integral over the square nearest the inner conductor is given first. Hence the capacitances per unit length (value of integral $\times 8 \times 1/4\pi$) may be evaluated and are 912.0 and 832.4 respectively. These compare favourably with the calculated values of 893.9 and 814.4 obtained by using a formula due to Bowman (1935), entailing an error of only 2 %.

conductors in ratio	values of integral				average
	1435	1432	1432	1431	
9:17	1435	1432	1432	1431	1432.5
1:2	1308	1307.5	1306	1308.5	1307.5

12. From the above it can be seen that in this type of problem attention is focused only on given values of the wanted functions round the boundary and not upon their normal gradients. This naturally simplifies the boundary conditions, and it is with curved boundaries that the simplification is greatest and most welcome.

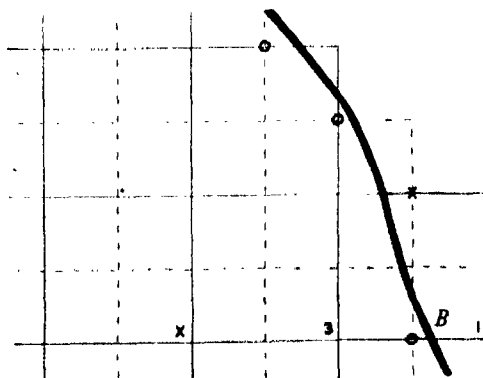


FIGURE 27. Curved boundary.

Consider, as an illustration, part of the boundary shown in the diagram (figure 27) along which ϕ is a constant. (An 'open' boundary would entail no greater difficulty.)

Thus at the points marked with a ring in the diagram, the residuals cannot be calculated because one or more of the required ϕ - or ψ -values is missing.

Whenever a ϕ -line cuts the boundary, let us produce it to the corresponding fictitious point; these fictitious points will form an outer boundary in the problem.

As explained in § 2, the value at such a fictitious point may be obtained in terms of the value at the boundary and the next two ϕ -points by the relation

$$\phi_1 = \frac{2}{\xi(1+\xi)}\phi_B + \frac{1-\xi}{1+\xi}\phi_X - \frac{2(1-\xi)}{\xi}\phi_a, \quad (21)$$

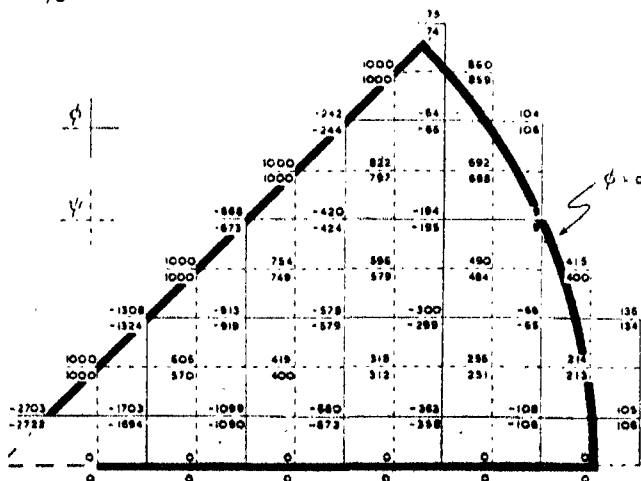
where the suffixes refer to the corresponding points in the diagram.

Thus the values at the fictitious ϕ -points may be obtained. The ψ -lines can be produced also to fictitious points with advantage in some instances, but it can be seen that this is necessary only when these points lie inside or on the 'outer' boundary formed by joining the ϕ -points. The values of ψ at such points will be found by the ordinary relaxation process, and no new features are there involved, although residual points may then be introduced outside the normal boundary of the figure, a typical example being indicated by a cross in the diagram (figure 27).

The example is really a test of this technique, and shows how it has been applied to the conformal transformation of a circular sector of angle $\frac{1}{4}\pi$ previously referred to in § 11. The same data were used, and the inner circle, on which there was only one point, a ϕ -point, was the 'open' boundary. Fictitious points were introduced outside the curved boundary, and treated as explained above. The result is shown in figure 28, and the values derived from the analytic solution of this problem, namely

$$\phi = \frac{4000}{\pi} \log_e \frac{r}{R} \quad \text{and} \quad \psi = \frac{4000}{\pi} \theta$$

are given for comparison in the same figure below those obtained by the relaxation method. It may be seen that they agree remarkably well, considering the coarseness of the net and the singularity of the solution at the origin, the greatest error being of the order of 5 %.



THE QUASI-PLANE-HARMONIC EQUATION

13. This equation which occurs frequently in problems in applied mathematics, is of the form

$$\frac{\partial}{\partial x} \left(\chi \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left(\chi \frac{\partial \phi}{\partial y} \right) = 0, \quad (22)$$

where χ is a known function of x and y , i.e. the values of the function for various values of x and y may be found, but clearly for this purpose, an analytic expression of the function is not necessary.

The equation lends itself to treatment by the technique of interlacing nets in a similar manner to the plane harmonic equation and the conjugate plane harmonic functions. A function ψ may be introduced by the relations

$$\chi \frac{\partial \phi}{\partial x} = \frac{\partial \psi}{\partial y} \quad \text{and} \quad \chi \frac{\partial \phi}{\partial y} = -\frac{\partial \psi}{\partial x}, \quad (23)$$

thus satisfying the equation (22) for ϕ .

The equation satisfied by the function ψ is

$$\frac{\partial}{\partial x} \left(\frac{1}{\chi} \frac{\partial \psi}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{1}{\chi} \frac{\partial \psi}{\partial y} \right) = 0, \quad (24)$$

and is also a quasi-plane-harmonic equation. It is from the equations (23) that the two wanted functions ϕ and ψ are found.

Using the two interlacing nets as before, the continuous line for ϕ and the broken line for ψ , a portion of the field may be considered with its typical ϕ , ψ and the A - and B -points as for the plane harmonic case (§ 9 and figure 21).

At the point A , labelling the four surrounding points 1, 2, 3, 4 with an effective mesh length a , and centred at the point A ,

$$\left(\frac{\partial \phi}{\partial x} \right) = \frac{1}{a} (\phi_1 - \phi_3), \quad \left(\frac{\partial \psi}{\partial y} \right) = \frac{1}{a} (\psi_2 - \psi_4).$$

Hence the first of the equations (23) becomes

$$\chi_A (\phi_1 - \phi_3) = \psi_2 - \psi_4,$$

where χ_A is the value of the function χ at the point A . This equation may be written as

$$F_A \equiv \chi_A (\phi_1 - \phi_3) - \psi_2 + \psi_4 = 0. \quad (25)$$

At the point B in a similar manner, expressions for $\partial \phi / \partial y$, $\partial \psi / \partial x$ may be obtained, and the second of equations (23) written as

$$\chi_B (\phi_2 - \phi_4) = -(\psi_1 - \psi_3) \quad \text{or} \quad G_B \equiv \chi_B (\phi_2 - \phi_4) + \psi_1 - \psi_3 = 0. \quad (26)$$

The relaxation patterns to be used are given in figure 29, and it can be seen that the function χ is involved in only one of the patterns, that for ϕ , and then in a very simple manner—the residual increment at any point is numerically the value of the function χ at that point.

The same 'sweep' of residual, first indicated in the patterns for the plane harmonic functions, is still present, and indeed most, if not all, of the technique involved there is still applicable here. Thus, for example, block-relaxation can be used as before, and the only residuals altered when such a block is applied are still those just outside the applied block.

As an illustration of the method the problem of heat conduction in a hemisphere composed of a central hemisphere of radius $2R$ with a concentric shell of thickness R , of different conductivities in the ratio 5 : 1 with its flat surface at 1000°C and its

$$\frac{\partial}{\partial r} \left(\kappa r \frac{\partial V}{\partial r} \right) + \frac{\partial}{\partial z} \left(\kappa r \frac{\partial V}{\partial z} \right) = 0$$

where κ is the conductivity and V the temperature.

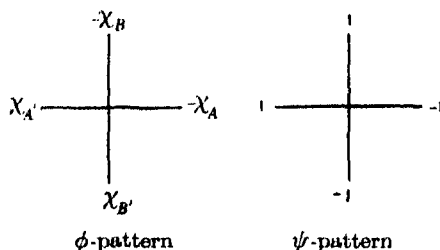


FIGURE 29. The relaxation patterns.

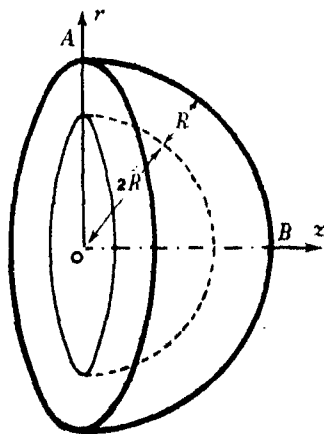


FIGURE 30

curved surface at 0°C (figure 30) was considered. The problem has axial symmetry, and using cylindrical co-ordinates the conduction of heat is governed by the equation

To make this equation non-dimensional, one may write $\kappa = k\kappa_0$, where κ_0 is the smaller conductivity considered, and then

$$\frac{\partial}{\partial r} \left(kr \frac{\partial V}{\partial r} \right) + \frac{\partial}{\partial z} \left(kr \frac{\partial V}{\partial z} \right) = 0.$$

An orthogonal function, ψ , the flux function, may be introduced such that

$$kr \frac{\partial V}{\partial r} = \frac{\partial \psi}{\partial z} \quad \text{and} \quad kr \frac{\partial V}{\partial z} = -\frac{\partial \psi}{\partial r}.$$

These equations are the typical quasi-plane-harmonic equations (23) and the known function $\chi = kr$. Taking a mesh length $a = \frac{1}{2}R$, a quadrant ABC was considered (figure 30), the boundary conditions being $V = 1000$ on AB , $\psi = 0$ on BC , $V = 0$ on CA and the open boundary a ψ -point at A . Fictitious points were introduced outside the curved boundary CA and treated as in § 12. The relaxation involved no great difficulty, and the solution is given in figure 31.

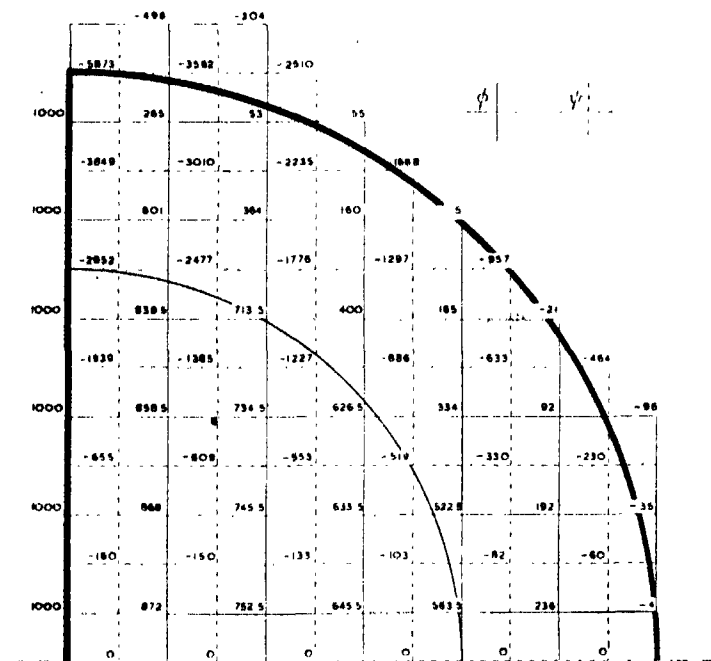


FIGURE 31. Conduction of heat in a hemisphere.

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The Wellcome Research Institution

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(*Lecture delivered 5 February 1948—MS. received 3 March 1948*)

[PLATES 5 TO 8]

The Wellcome Research Institution is the name which Sir Henry Wellcome used to describe collectively the Museums and the various research undertakings of the Wellcome Foundation Ltd. Before outlining the development of the individual units I must first briefly relate the history of the Wellcome Foundation itself.

The firm of Burroughs Wellcome and Co. was founded in London in 1880 by two young American pharmacists, Silas M. Burroughs and Henry S. Wellcome. This proved a most successful undertaking, and after the death of Burroughs in 1895 Wellcome became the sole owner of a flourishing business with commercial offices in Snow Hill, chemical works at Dartford and the beginnings of his earliest research enterprise, the Wellcome Physiological Research Laboratories.

The next 30 years saw the development not only of the business in this country but of associated houses in U.S.A. and other parts of the world, and in 1924 Wellcome consolidated all his interests in a single company, the Wellcome Foundation Ltd. This fusion was done with a deliberate purpose later to be revealed by his will. Within the framework of the business itself he had already developed the laboratories for scientific research and the educational museums that I shall presently describe. Beyond these the will provided for scientific work outside the business itself, for, on Wellcome's death in 1936, all the shares in this Company were vested in five trustees who were to receive the whole of the distributable profits and use them in certain specified ways for the advancement of research in medicine and its related subjects anywhere in the world.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES

When diphtheria antitoxin first came into use Mr Wellcome realized its importance and in 1895 set up laboratories in London for its manufacture. In 1898 these were moved to Brockwell Hall, Herne Hill, which, with 10 acres of ground, stabling and other buildings, provided suitable accommodation not only for the manufacture of the new serum but for the more ambitious research projects Mr Wellcome had in mind. These were foreshadowed by the name he gave the laboratories in 1895.

The research history of this unit did not commence until the beginning of the present century, when, in spite of opposition by the Royal Colleges of Physicians and Surgeons, the premises at Brockwell Hall were registered as a place where

experiments on living animals might be performed. This was the first instance of such recognition for laboratories attached to a commercial firm.

During 52 years this unit has had three periods of active research interrupted by two world wars, during each of which nearly all research, except what was essential to production, ceased. During the first period from 1900 to 1914 the laboratories were directed first by Dr Walter Dowson till 1906 and then by Dr H. H. Dale till the outbreak of the first world war.

Dr Walter Dowson, though not himself an experienced scientific worker, was a capable administrator who succeeded in attracting young and well-trained scientific personnel and in creating good conditions of work for them. Among the early members of the scientific staff were a number of men who subsequently became Fellows of this Society—George Barger, H. H. Dale, A. J. Ewins, A. T. Glenny, P. P. Laidlaw and John Mellanby, and at a somewhat later period, Harold King and J. H. Burn.

John Mellanby was the first pharmacologist appointed to the laboratories and spent several years there in studying the globulins and other proteins from horse plasma and serum. He described a method for concentrating diphtheria antitoxin without denaturation of the protein by treating the serum with alcohol at low temperatures—a principle which has recently been brilliantly developed and extended by Cohn and his colleagues at Harvard.

A. T. Glenny, who only last year retired from the staff, controlled the production of antisera at the laboratories for about 40 years but found time to utilize for research the wealth of material which was available to him as well as to carry out well-planned experiments on immunity.

The association of Barger, Dale, Ewins and Laidlaw during these early years was a most fruitful one. When Dale joined the staff as pharmacologist in 1904 Barger had already commenced the investigation of ergot which not only yielded valuable direct results but led to studies of even greater importance. The alkaloid, ergotoxine, was discovered through the recognition of its curious action of adrenaline reversal. Histamine, which in the intervening years has proved to be of great interest in relation to anaphylaxis and various shock-like conditions and in the immediate reaction to injury, was isolated from extracts of ergot and its pharmacological action was analyzed by Dale and Laidlaw. Other amines also engaged attention, and Dale and Barger made an extensive study of the relation of their chemical structure to sympathomimetic action.

The action of ergot in causing strong contraction of the uterus led Dale to the study of another powerful oxytocic present in extracts of the posterior lobe of the pituitary gland. This work formed the basis for the method of standardizing such extracts described by Dale and Laidlaw which is still in general use.

The observation that a particular ergot extract had peculiar properties led to the identification in it of acetylcholine by Ewins. The discovery by Dale of the muscarine- and nicotine-like activities of this substance, by which it simulated effects of different groups of efferent nerves, provided the foundation for studies

later resumed by Dale and his colleagues at the National Institute; these, with the researches of Otto Loewi, played a formative part in the modern conception of the chemical transmission of nervous stimuli.

Other important researches were the examination of the anaphylactic response of the uterus of the sensitized guinea-pig by Dale and investigations of the hydrogen-ion concentration of biological fluids by G. S. Walpole, who first organized the concentration of antitoxin at the laboratories.

The scientific staff at this time was small, less than a dozen, but they were a very active group, and during this period about 100 papers, many of them of classical importance, were published.

The year immediately preceding the outbreak of the first world war broke up this happy company. Laidlaw went to the professorship of pathology at Guy's and Dale joined the research team which was being built up by the Medical Research Council, taking with him Barger and Ewins. Dale was succeeded by Dr R. A. O'Brien who, with a greatly reduced scientific staff, was confronted by the wartime problem of a large increase in production. During the war the production demand was fully met and large quantities of tetanus and diphtheria antitoxins, antigangrene sera and typhoid vaccines were made available for the forces.

Shortly after the war Mr Wellcome bought a property of rather more than 100 acres at Langley Court, Beckenham (figure 2, plate 5), and the move there was made in 1922. During the period between the two world wars the scientific staff gradually increased in number, reaching a total of 28 in 1939. Of the staff in this interwar period three more were later to become Fellows of this Society—Percival Hartley, J. H. Gaddum and J. W. Trevan.

Between 1921 and 1939 over 300 papers were published. Glenny now had his most productive period. He had already discovered the difference in effect between primary and secondary stimuli in active immunization, though the publication of this work had been delayed, and he now contributed year by year a series of papers on active and passive immunization mainly concerned with the response to diphtheria toxin. With Pope and Miss Hopkins he was early in the field in the conversion of toxin to toxoid by formaldehyde, and he and his colleagues discovered the advantageous effect of precipitating toxin with alum. Alum-precipitated toxoid (A.P.T.), and indeed other alum-precipitated toxoids, have since been very widely used for immunization.

O'Brien was the first in this country to carry out Schick testing and was a pioneer advocate of active immunization against diphtheria. Dalling's work contributed much to the control of lamb dysentery, a disease which formerly killed many thousands of lambs each year in Britain. He identified the causative organism and showed that the pregnant ewe could be actively immunized by vaccination and could transmit effective immunity to its offspring. With Glenny he elaborated an antitoxic serum for the passive protection of newly born lambs.

Hartley during 1920 and 1921 developed a medium for the production of diphtheria toxin which has found worldwide use and made possible uniform production of

potent diphtheria toxin. This work has been the basis of the great improvements in toxin production which have been made since that time. He was also a pioneer in the rapid drying at low temperatures of sera and other protein solutions, developing a method which he found most useful during the next 25 years when he was in charge of the Standards Laboratory at the National Institute for Medical Research.

Dalling made generally available the method of immunization against dog distemper which has been developed by the researches of Laidlaw and Dunkin at the National Institute for Medical Research.

Pope made an important contribution in developing a method for concentrating antitoxic sera which depended upon preliminary digestion and heat denaturation of unwanted proteins. The use of this and other methods of serum concentration has greatly diminished the incidence of serum sickness after the therapeutic use of antitoxin.

During this period much attention was directed to accurate methods of standardization of therapeutic substances, and Trevan, in 1927, published an important paper on the statistical basis of determinations of the lethal dose and other biological end-point reactions, which has had a wide influence on the design of methods of bio-assay.

During the period immediately before the second world war Buttle and his associates were actively engaged in studies on chemotherapy, particularly on sulphone derivatives and sulphonamide.

During the early part of the recent war, under the direction of Dr R. A. O'Brien and after 1941 under Dr J. W. Trevan, the laboratories were faced with an even larger production demand than in the first world war. Vast quantities were made and issued of tetanus and gas gangrene antitoxins, tetanus toxoid, and the major part of the diphtheria prophylactics used by the Ministry of Health in its free immunization campaign. Additional laboratory accommodation was needed and the L.C.C. made available their laboratories at Carshalton and Belmont. Over 1000 horses had to be maintained for the manufacture of sera and stabling accommodation was acquired in various parts of the country, some even so far afield as Doncaster. When the Veterinary Research Station was established at Frant, in Sussex, in 1943 some further stabling accommodation had to be provided there.

During the latter part of the war a large mechanical surface culture plant was set up at Beckenham for the manufacture of penicillin, but in 1945, when it became apparent that manufacture by the bottle process could not compete economically with deep culture, its use was discontinued. Before it was closed down some streptomycin was produced for experimental purposes in a portion of the plant. Work on antibiotics was now confined to search for new ones in a small unit at Belmont, which had been used for the manufacture of penicillin, and later in the main laboratories at Beckenham.

At the end of the war diminished production again made possible increased research activity and there has been a large increase in the number of papers issuing from these laboratories. The most important recent work of which mention

should be made are further studies on immunity, on the toxins of the *Cl. welchii* group, on the pharmacology of 'Sulphetrone' and streptomycin, work on the production of diphtheria toxin by deep culture, the development of a new method of refinement applicable to antibacterial sera which depends on precipitation with ammonium sulphate in the presence of tricoresol, and studies on 'Aerosporin', a new antibiotic which covers part of the bacterial spectrum not adequately covered by either penicillin or streptomycin. Aerosporin appears not readily to allow of the production of resistant bacterial strains, and gives promise of real value in the treatment of whooping cough and of some other diseases caused by Gram-negative organisms.

THE WELLCOME VETERINARY RESEARCH STATION

By the end of 1943 it had become apparent that the property at Beckenham was not adequate for the satisfactory breeding of the large number of small animals needed for testing and research, and a farm of more than 300 acres was purchased at Ely Grange, Frant (figure 7, plate 8). Here small animals could be bred under isolated conditions, particularly ferrets for developmental research on distemper products. Here too the green food needed for stock animals and those under experiment at Beckenham could be grown and a suitable place was provided for the investigation of diseases of larger animals, particularly of sheep and cattle. The scientific staff, under the direction of Dr R. F. Montgomerie, has ranged from three to six in number and the chief problems so far studied there have been mastitis in milking herds, bovine infertility, problems connected with small animal breeding and the study of immunity against louping ill. At the end of 1946 a temporary Artificial Insemination Centre was set up there in collaboration with the Milk Marketing Board.

The smooth development of the Frant farm as a veterinary research station suffered somewhat from the war enterprise given the secret name of the 'Tyburn' operation, which was carried out there in 1945. By the end of 1944 it had become apparent that scrub typhus might be a serious menace to jungle operations in south-east Asia and elsewhere, and the War Office decided to have made on a large scale the scrub typhus vaccine which had been devised by Fulton and Joyner at the National Institute for Medical Research using the lungs of cotton rats infected with the causative rickettsiae. The Ministry of Supply with the advice of the Medical Research Council requested the Wellcome Foundation to undertake this task and the Medical Research Council seconded to us Dr M. van den Ende to take charge of the scientific side of the operation and direct the developmental and other researches which were carried out during its progress. The manufacture of the vaccine involved the importation by air from America of thousands of cotton rats and the simultaneous breeding of large numbers of these animals in this country. Ely Grange, Frant was selected for the enterprise as being sufficiently isolated and as providing accommodation for the workers engaged in a difficult and dangerous project. The scientific personnel, nine in number, were partly civilian and partly

officers of the R.A.M.C. and the A.T.S. and the sixty technical personnel were R.A.M.C. laboratory technicians and A.T.S. who volunteered for the work.

The laboratories were built in 109 days and the preparation of vaccine was started on 1 May 1945. Between that date and 31 October, when manufacture was discontinued, 300 l. of vaccine, enough to vaccinate 100,000 men, were made. This was a highly dangerous technical operation involving inoculation of cotton rats by insufflation with a seed suspension of rickettsiae from the lungs of mice infected in the same way. The rats were kept for several days and died or were killed, the lungs being harvested and emulsified to make the vaccine which was treated with formalin to kill the rickettsiae. The workers engaged in the manufacture were vaccinated and the most dangerous operations were carried out in cabinets ventilated by suction, the air from these being sterilized by special furnaces on the roof of the laboratories. A good many other precautions were used—the air in the laboratories was treated by aerosols of lactic acid and very carefully controlled procedures were laid down to minimize risk. Despite these precautions, four workers were accidentally infected. All had, of course, been protected by vaccination and fortunately made uneventful recoveries.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES

These Laboratories were founded in London in 1896 and remained at 6 King Street, Snow Hill for 35 years. In 1923 they were transferred to the new building of the Wellcome Research Institution at 183 Euston Road where a portion of the staff is still housed as part of the Laboratories of Tropical Medicine (figure 5, plate 7).

When the Laboratories were founded, Mr Wellcome persuaded his friend, F. B. Power, to come over from America and take charge of them. During Power's directorship work was mainly concentrated on increasing systematic knowledge of the chemical constituents of plants used in medicine, and a wide range of these was investigated. During this period in the development laboratories at Dartford Dr H. A. D. Jowett carried out his work on the constitution of pilocarpine which was shown to contain a glyoxaline nucleus, Dr F. L. Pyman synthesized two other physiologically important glyoxaline derivatives, histidine and histamine, and Jowett and Pyman did their work on the tropine esters.

When Pyman followed Power as Director of the Chemical Research Laboratories in 1914 attention was focused on synthetic drugs and alkaloids. Pyman continued the fruitful studies commenced at Dartford on the ipecacuanha alkaloids. Dr Harold King carried out his important work on the resolution of the optically active components of hyoscyne. The Laboratories during the first world war were also faced with the problem of devising means of replacing German synthetic drugs, the most important of which was arsphenamine.

When Dr Henry became Director in 1919 the main interest of the Laboratories was turned towards the chemotherapy of tropical disease. Some synthetic compounds were prepared for the treatment of hookworm and the investigation of

chenopodium oil which was being extensively used for this purpose showed that its only active component was ascaridole. Work on the antimony compounds for the treatment of kala azar resulted in the synthesis of the *N*-glucoside of *p*-aminophenyl stibonic acid ('Neostam'). Just before the second world war a new pentavalent antimony compound was devised in Germany for the treatment of kala azar, and early in the war the composition of this drug was determined and a process designed for its manufacture.

Work on antimalarials included an extensive investigation of the alkaloids of the genus *Alstonia* and a study, carried out on behalf of the Malaria Commission of the League of Nations, of the composition and standardization of the quinine alkaloids.

The 4-4'-diaminodiphenylsulphone derivative, 'Sulphetrone', which shows promise in the treatment of leprosy was also synthesized in these laboratories.

Meanwhile at the Development Laboratories at Dartford, under Dr Sydney Smith's direction, research on ephedra led to the isolation of two new alkaloids. Here too Dr Smith isolated digoxin, the pure crystalline glucoside of *Digitalis lanata*.

When Dr Henry retired in 1944 Dr Smith took charge of the main laboratories which were to be established at Beckenham when the new building (figure 6, plate 7) was completed. In the meanwhile accommodation was found for Dr Smith and three of his colleagues in one of the more modern laboratories at Langley Court where this team worked on penicillin synthesis making an important contribution in the isolation of penicillic acid. The move into the new building took place in 1946, a portion of it being used to house part of the chemotherapeutic testing unit.

The new laboratories have been working for too short a period for more than the most general report of their activities to be made. A number of new phenanthridinium compounds, active against more than one species of trypanosome, have been synthesized, interesting studies have been made on the chemistry of the new antibiotic, Aerosporin, and work on substitutes for *d*-tubocurarine and on analgesics and antiasthmatics has been in progress.

THE WELLCOME LABORATORIES OF TROPICAL MEDICINE

Mr Wellcome's first venture into tropical research was conducted to some extent vicariously. In 1901 he offered to the Gordon Memorial College, Khartoum, equipment for chemical and bacteriological laboratories, the College being responsible for the building and for the selection and support of the scientific staff. The Wellcome Tropical Research Laboratories so founded continued until 1935 when they were closed down by the Sudan Government, the space occupied by them being needed for other purposes. The first Director of these Laboratories was Dr Andrew Balfour. In 1907 Mr Wellcome provided a floating laboratory to carry research to regions which were otherwise not readily accessible and Dr C. M. Wenyon was placed in charge of this.

In 1913 the Wellcome Bureau of Scientific Research was founded with Andrew Balfour as Director and as Director-in-Chief of all the various research units which

Mr Wellcome had set up. The Bureau was to be a centre in London for the study of tropical disease with the important function of supplying information to workers abroad, and its staff included C. M. Wenyon as protozoologist, A. C. Stevenson as pathologist and M. E. MacGregor as entomologist.

Shortly after the Bureau had been established the first world war broke out and the Bureau was placed at the disposal of the War Office. It played an important part in training medical officers in tropical disease and Dr Balfour wrote the well-known 'Memoranda on Medical Diseases in the Tropical and Sub-Tropical War Areas'. Balfour and Wenyon spent most of the war years at various fronts mainly acting as consultants; and Wenyon did his important work on amoebic dysentery in Egypt and on malaria in Macedonia.

During the war the development of the Bureau was necessarily inhibited, but when the war ended its staff was increased and in 1920 it moved from Henrietta Street to more commodious premises at Endsleigh Gardens. From this time till the present it has had generally 9 to 11 senior scientific workers on its staff.

In 1923 Balfour resigned, becoming Director of the newly-created London School of Hygiene and Tropical Medicine, and Wenyon succeeded him as Director of the Bureau of Scientific Research and Director-in-Chief of the Wellcome Research Institution. The policy was followed of seconding workers to various laboratories abroad; for example, in 1927 C. A. Hoare went to work on trypanosomiasis in the Sleeping Sickness Laboratory at Entebbe, and later G. M. Findlay made numerous ventures in different parts of the world to study yellow fever and other diseases. The Bureau was also available for guest workers, and it is of interest that in 1928 Dr E. Hindle began there his work on yellow fever for the Yellow Fever Commission of the Colonial Office, in which he carried out the first preventive vaccinations on monkeys with formalized virus.

In 1932 the building in the Euston Road (figure 1, plate 5) was erected to house the Museums, the Bureau and the Chemical Research Laboratories. In their new quarters work was now begun on virus diseases, and on leptospiral infections. The manufacture of yellow fever vaccine on a laboratory scale was started by G. M. Findlay, who had visited the United States to study the methods of research and manufacture at the Rockefeller Institute. Numbers of service personnel were inoculated year by year and, when the second world war broke out, free inoculation was continued on a large scale subsidized to some extent by the Colonial Office until the end of the war.

The problem of infective hepatitis and of serum jaundice had in the intervening years engaged the attention of workers at the Bureau and during the war F. O. MacCallum was seconded to work at Cambridge on a special enquiry concerning infective hepatitis, financed by the Medical Research Council.

In 1944 Dr Wenyon retired and the departmental controls were reorganized. I joined the staff as Director-in-Chief and Dr N. H. Fairley was invited to become Director of the Laboratories of Tropical Medicine and also professor in the new Chair of Tropical Medicine founded by the Wellcome Trustees at the London School of

Hygiene and Tropical Medicine. Fairley, however, found himself so fully occupied by his professorial duties that he resigned and was succeeded late in 1946 by Brigadier J. S. K. Boyd who had just retired from the directorate of pathology at the War Office.

The Bureau of Scientific Research, or to use its present name, the Wellcome Laboratories of Tropical Medicine, during its 34 years existence has had a distinguished record in research in tropical disease, and 8 books and more than 560 papers have been contributed by members of its staff, the most important being C. M. Wenyon's classical *Manual of Protozoology* published in 1926.

The main problems on which work is now in progress concern bacteriophages, the tissue culture of protozoa, the serology of leptospirosis and the chemotherapy of tropical diseases (figure 4, plate 6).

The policy of sending workers abroad is being continued—Dr J. M. Watson having spent most of last year in Egypt studying bilharzia, a member of the Egyptian State Health Service having been an exchange guest worker in the laboratories here.

Closely associated with the Bureau are the Entomological Field Laboratories which were opened at Wisley in 1920 by Mr M. E. MacGregor. In 1921 the laboratories were moved to new premises at Esher in Surrey where for the last few years Mr B. Jobling has been carrying on his beautiful anatomical and histological studies on the blood-sucking diptera. At the present time when other large and well-equipped laboratories for entomological study are available in this country there seems little justification for the continuation of this small unit.

THE WELLCOME MUSEUM OF MEDICAL SCIENCE

The Museum of Medical Science arose primarily from the interest of Andrew Balfour in teaching museums. He had started such a museum at Gordon College and as soon as he took charge of the Bureau in 1913 he commenced to develop one there. The real history of the Museum began when Dr S. H. Daukes, who had been appointed Curator in 1919, became Director of the Museum and in 1923 extended its scope to include diseases of temperate as well as tropical climates with the object of presenting an up-to-the-moment picture of advances in medicine.

The Museum grew rapidly and in 1932 three spacious galleries (figure 8, plate 8) were provided for it in the new building in Euston Road. Here Dr Daukes set it out in admirable fashion and secured a wealth of material illustrating the aetiology, symptomatology, pathology, treatment and prevention of disease. There were also sections on general and special pathology. The Museum was increasingly used by students, doctors, and nurses and others and in the year before the second world war began it had over 10,000 visitors.

After the outbreak of the second world war, when it appeared likely that London would be bombed, the Museum was dismantled and the valuable collection stored. In 1945, when this threat was removed, it was possible to re-establish it in part

despite considerable damage to screens and windows caused by neighbouring bomb explosions. A beginning was made with the East wing, in which much of the tropical material is set up, and Dr Daukes was able to complete this before he retired at the end of 1945. He was succeeded by Dr C. J. Hackett, who, before continuing the establishment of the Museum, decided to modernize its presentation. The system introduced by Daukes could not be bettered, but improvement in lighting, with re-arrangement enabling visitors more readily to grasp the essential features, will undoubtedly increase the value of this much-used collection. It will unfortunately be several years before the Museum is complete and up-to-date in every part.

THE WELLCOME HISTORICAL MEDICAL MUSEUM

The story of the development of this museum is really a part of the story of Henry Wellcome's life. In 1905, having arranged his affairs so as to obtain more leisure, he started collecting all kinds of material connected with the history of medicine, and the idea of creating a great museum of medical history became his keenest interest till the end of his life.

In 1913, he found housing for his collection in Wigmore Street, and displayed there much of his best material. The collection, which was used for a number of important exhibitions, remained there till 1932, when the new building in Euston Road was ready for its reception. From 1924 onwards Sir Henry Wellcome devoted increasing time and energy to the collection of material. After the move to the new building the Museum was not at once opened, but the work of sorting the material was begun. Sir Henry Wellcome, who had just been elected a Fellow of this Society, had hoped finally to settle the layout, but he died in 1936 with his plan for this still uncompleted.

In his lifetime Sir Henry Wellcome himself was Director of this Museum and it was not till 1943 that Dr Daukes, who till his retirement in 1945 acted as Director of both Museums, proposed a plan for its re-arrangement when this could again be undertaken. At the end of 1945 this plan was in the course of being put into effect. In 1946 Dr E. Ashworth Underwood, a distinguished scholar of medical history, was appointed Director in succession to Dr Daukes and made plans to open not only the Museum but also the Library of 150,000 volumes, which till then had not been available for consultation, the work of cataloguing it being only about two-thirds completed.

Unhappily last year the Museum had a further and most disappointing setback, which will delay for some years its establishment in the building in which Wellcome had planned to house it. In 1940 when the central offices of the business at Snow Hill were completely destroyed it was necessary that its administrative staff should be given immediate accommodation within the building in Euston Road. This was not a serious matter during the war, since considerations of safety of the valuable material limited the use of the galleries as a Museum. In due course premises were found on short lease for housing most of the business and administrative staff, in

the expectation that at the end of the war new accommodation could be built to take the place of the offices destroyed by enemy action.

When in 1947 the temporary lease of these premises came to an end, prolonged and active search during two years through the whole of London for suitable premises having failed and the prospect of building new offices being removed to an uncertain future, nothing remained but to house the business activities in the building in Euston Road and to put most of the Museum material into store, until such time as the galleries once more become available for its display.

Fortunately, however, the Wellcome Trustees have been able to secure accommodation to house Dr Underwood and the Museum staff, and to afford them opportunity to continue their researches, as well as to give limited public exhibitions of valuable parts of the collection from time to time. The Library, though not ideally set up, remains in the Euston Road building and will be available for consultation by scholars interested in the history of medicine.

Having now traced the history of this rather complex research organization which Henry Wellcome built up it remains to get its structure into perspective and to indicate the causes of its early success. Wellcome was an autocrat and during his lifetime rigidly controlled the organization in the directions he desired. He early recognized the importance of scientific research for the development of his business interests and in the process gained an enthusiasm for the application of science in all three of the ways Sir Edward Appleton has recently described, 'applied research, objective fundamental research and free fundamental research'. The scientific workers whom he engaged were allowed to work largely on subjects of their own choice although he sometimes suggested topics in which he was particularly interested. They were also at liberty to publish the results of their researches and were thus not detached by rules of secrecy from their academic colleagues. This, fifty years ago, must have been an unusual situation to be occupied by men who had been attracted to industrial laboratories. The application of this policy was in the main responsible for the scientific distinction of the workers in the laboratories and for the high reputation of the laboratories themselves.

Wellcome's interest in education resulted in the development of the Museum and Library of Historical Medicine, the Bureau of Tropical Medicine and the Museum of Medical Science. The close collaboration of these last two units with the Tropical Diseases Hospital and the London School of Hygiene and Tropical Medicine has helped to make London an important centre for the study of tropical disease.

Though these educational units were within the framework of the business, Wellcome made some attempt to set them apart when he designed the great building in Euston Road to house them, but the second world war and its aftermath have prevented the smooth development of his large conception.

In the meanwhile the research organization must be directed towards increasing the prosperity of the business and the funds available to the Trustees for the broad purposes indicated by the Founder's will. In this country the Foundation has extensive and well-equipped laboratories and at the present time has a staff of

about 80 graduate scientific workers, a large number of skilled technicians and many young men and women who are acquiring university degrees while they are engaged as technical assistants. This does not include the staff of the Chemical and Pharmaceutical Development Laboratories at the Works at Dartford who are responsible, under the direction of Dr Denis Wheeler, for the improvement of the processes in operation there as well as for development to the stage of production of projects handed over by the research staff. On the biological side there is no segregation of development and a good many of the scientific workers at the Beckenham laboratories are engaged in production of biological products for the improvement of which continuous developmental work is required.

As the research organization increased in size there was until recent years some tendency for units, and even for departments within units, to work independently. This has been discouraged and a degree of plasticity has been achieved which enables a number of workers to be concentrated on any urgent problem. Our current researches are co-ordinated with those being carried out in the research unit in our New York company and each part of the organization is being made aware of what is going on elsewhere. This important objective is being achieved by the circulation of regular reports on the progress of research projects, by visits between the units and by annual research meetings, attended by all the workers at which the current researches are reviewed and new projects indicated. In addition to these more general meetings the workers engaged in each project meet for frequent consultation and from time to time their projects are reviewed more formally, in the light of the current project reports, by myself and the heads of the research units concerned.

Publication remains free and is encouraged, and, though the bulk of work done is directed specifically towards the discovery of new therapeutic agents and therefore comes into the category of applied research, fundamental studies of the objective type form an important part of our programme.

DESCRIPTION OF PLATES 5 TO 8

PLATE 5

FIGURE 1. The building of the Wellcome Research Institution, 183 Euston Road, N.W. 1.

FIGURE 2. Aerial view of the Wellcome Research Laboratories, Langley Court, Beckenham, Kent. Wellcome Physiological Research Laboratories 1 to 9 and 11. 1, Penicillin building; 2, Administration block; 3, Biochemistry laboratories; 4, Pharmacology laboratories; 5, Immunology laboratories; 6, Veterinary department; 7, Bacteriology laboratories; 8, Media Production Unit; 9, Chemotherapy section; 11, Veterinary stables; 10, Wellcome Chemical Research Laboratories.

PLATE 6

FIGURE 3. A laboratory for chemotherapy of tuberculosis at the Wellcome Physiological Research Laboratories.

FIGURE 4. A laboratory for chemotherapy of tropical diseases in the Wellcome Laboratories for Tropical Medicine.

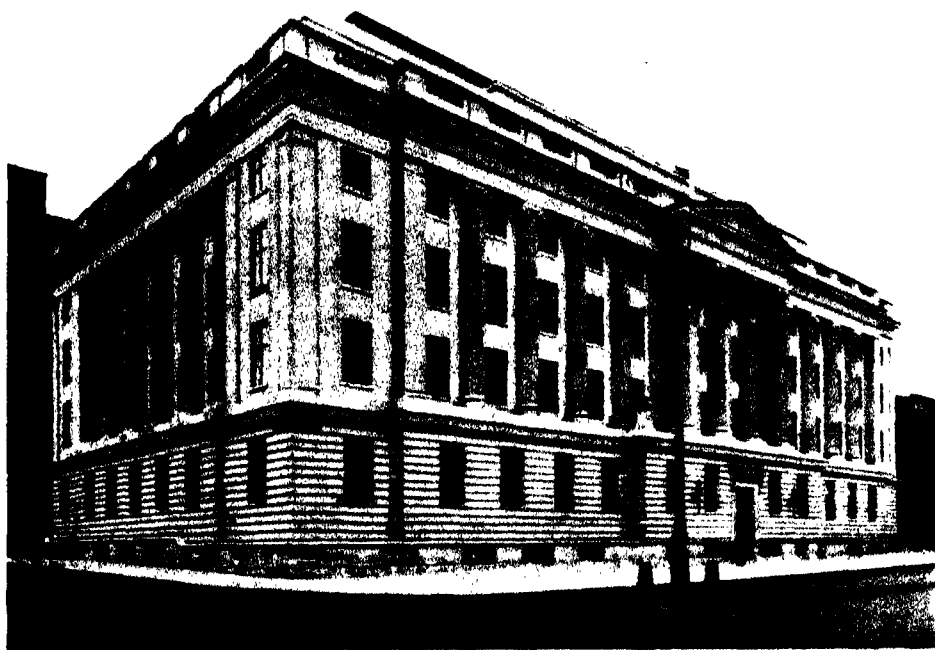


FIGURE 1

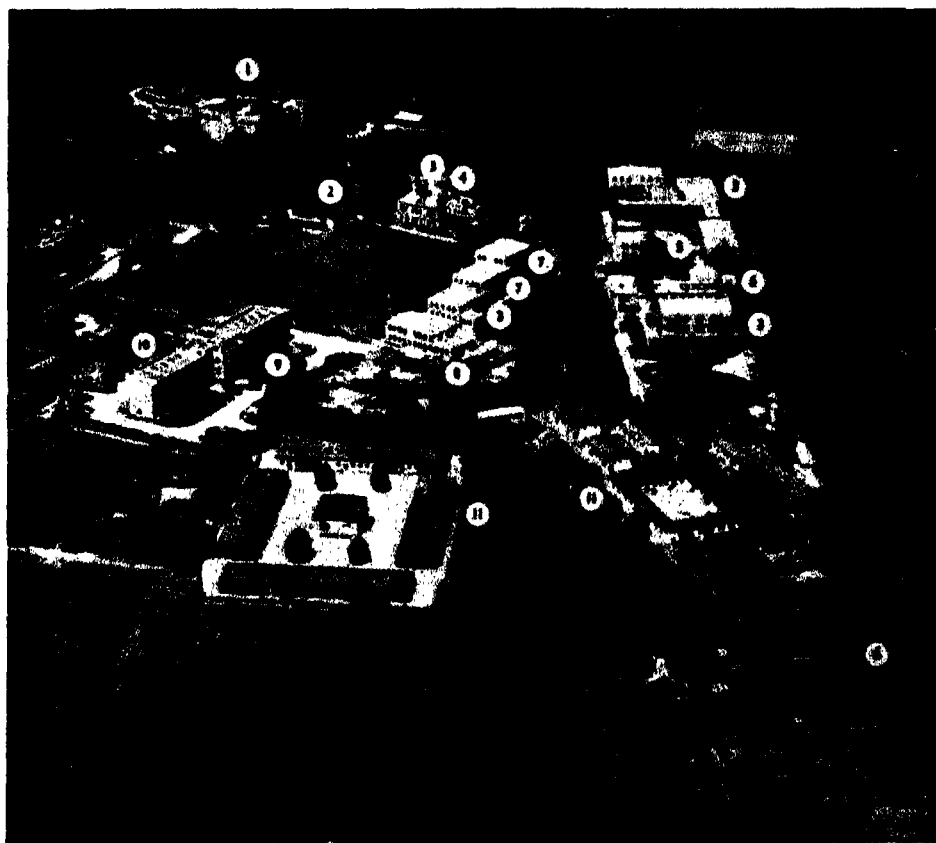


FIGURE 2



FIGURE 3



FIGURE 4



FIGURE 5



FIGURE 6

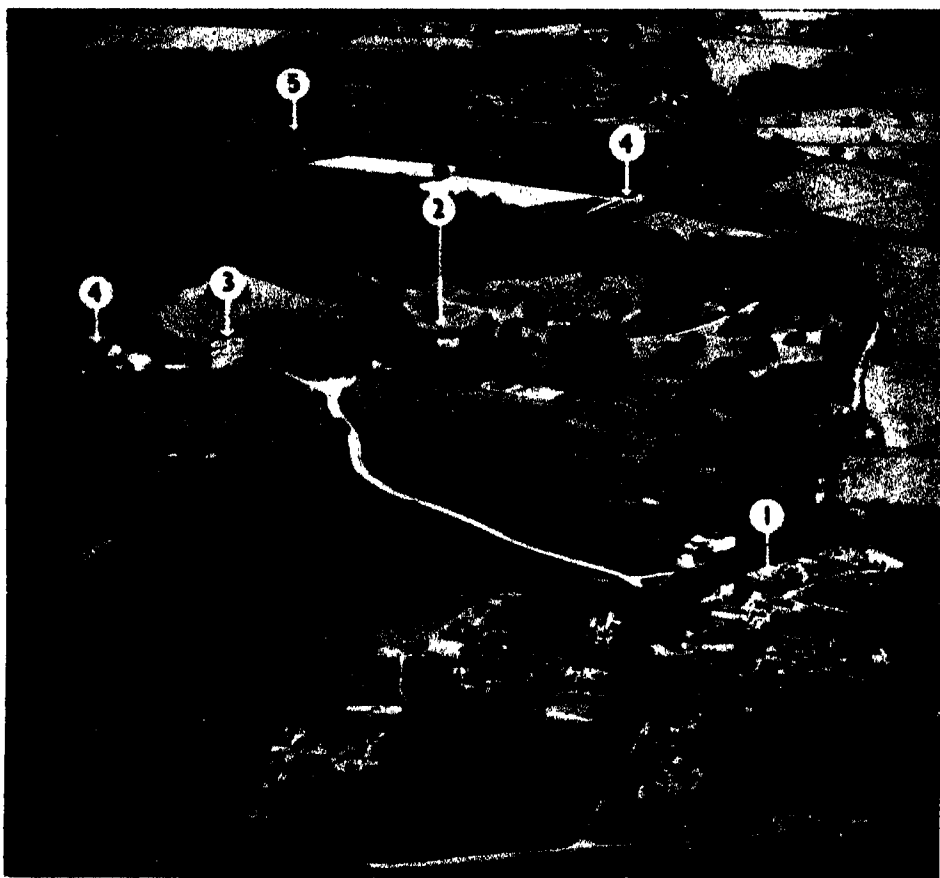


FIGURE 7



FIGURE 8

PLATE 7

FIGURE 5. A chemical laboratory in the Wellcome Laboratories for Tropical Medicine.

FIGURE 6. The Wellcome Chemical Research Laboratories, Langley Court, Beckenham.

PLATE 8

FIGURE 7. Aerial view of the Wellcome Veterinary Research Station, Ely Grange, Frant, Sussex. 1, Farm buildings; 2, Ely Grange; 3, 'Tyburn'; 4, Small animal breeding units; 5, Stables.

FIGURE 8. A portion of the Wellcome Museum of Medical Science at 183 Euston Road, N.W. 1.

The electronic structure of conjugated systems.

Parts III and IV

III. Bond orders in unsaturated molecules

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This part is concerned with the changes in bond order that take place in a conjugated system when the resonance integral of a bond, or the coulomb term of an atom is altered. It is shown that the sign of the mutual polarizability of two bonds in a chain depends upon whether there is an even or odd number of other bonds between them. Numerical values are given for mutual bond polarizabilities in some important hydrocarbons, and it is found that in the polyenes the effect of a perturbation decreases rapidly with distance along the chain. The effect of hetero-substitution on bond orders is considered, and the results compared with the predictions of the qualitative resonance theory.

INTRODUCTION

The definitions of mobile bond order and total bond order given in part I were originally introduced by Coulson (1939), who calculated bond orders for a number of unsaturated hydrocarbons and found a smooth relation between bond order and bond length. In this paper we shall be primarily interested in changes in bond order, consequent upon changes in Coulomb terms or resonance integrals. Such changes occur when, for example, a molecule vibrates, owing to the variation of resonance integral with bond length, or when one or more atoms in a molecule are altered, as in chemical substitution. In this investigation we shall use the notation and nomenclature given in part I of this series; in particular, the concept of mutual bond polarizability is helpful when we are discussing changes in bond order arising from

small changes in bond length. It is therefore convenient to begin by establishing a few general results about mutual bond polarizabilities: in parts IV and V these results will be applied quantitatively to particular problems.

VARIATION OF BOND ORDERS WITH RESONANCE INTEGRALS

In the previous part it was shown that in a rather special type of hydrocarbon—conveniently described as an alternant hydrocarbon—the mutual polarizability of two atoms was positive or negative according as the atoms were separated by an even or odd number of unsaturated bonds. A similar result will now be proved about the mutual polarizability of two bonds in an alternant hydrocarbon.

Let $\Delta^{(n)}$ denote the secular determinant for an alternant hydrocarbon with n unsaturated carbon atoms. Then if n is even, $\Delta^{(n)}(iy) = \Delta^{(n)}(-iy)$, by equation (5), part II. Therefore if y is real, $\Delta^{(n)}(iy)$ is real. But Δ has no zeroes on the imaginary axis, by hypothesis; therefore $\Delta^{(n)}(iy)$ is constant in sign. But the first term in $\Delta^{(n)}(iy)$ is $(-iy)^n$. Therefore if $n = 4p$, $\Delta^{(n)}(iy)$ is real and positive, whereas if $n = 4p + 2$, $\Delta^{(n)}(iy)$ is real and negative. On the other hand, if n is odd, $\Delta^{(n)}(iy)$ is iy times some real polynomial in y^2 , since $\Delta^{(n)}(iy) = -\Delta^{(n)}(-iy)$. Now $\Delta^{(n)}(iy)$ is zero at the origin, but nowhere else on the imaginary axis; therefore the real polynomial is constant in sign. But the first term of $\Delta^{(n)}(iy)$ is $(-iy)^n$; therefore if $n = 4p + 1$, $\Delta^{(n)}(iy) = -iyP$, where P is a real positive function, whereas if $n = 4p + 3$, $\Delta^{(n)}(iy) = iyP$, where P is real and positive. To summarize, $\Delta^{(n)}(iy) = P, -iyP, -P$ or iyP according as $n \equiv 0, 1, 2$ or 3 (modulo 4), where P is real and positive for all real values of y . (1)

It follows that $\Delta^{(m)}(iy)/\Delta^{(n)}(iy) = Q, iyQ, -Q$ or $-iyQ$ according as $n - m \equiv 0, 1, 2$ or 3 (modulo 4), where Q is real and positive for all real values of y except possibly $y = 0$, where it may become infinite. (2)

Now consider a conjugated system containing two bonds rs and tu such that all routes from atom r to atom u traverse atoms s and t (see figure 1). Let l be the number of bonds along any route between atoms s and t . Then by I (78)

$$\left. \begin{aligned} \Delta_{r,t} &= (-)^{r+t} \sum (-\beta)^{l+1} \Delta^{(n-l-2)}, \\ \Delta_{s,u} &= (-)^{s+u} \sum (-\beta)^{l+1} \Delta^{(n-l-2)}, \\ \Delta_{r,u} &= (-)^{r+u} \sum (-\beta)^{l+2} \Delta^{(n-l-3)}, \\ \Delta_{s,t} &= (-)^{s+t} \sum (-\beta)^l \Delta^{(n-l-1)}, \end{aligned} \right\} \quad (3)$$

and

the summations being taken over all routes between atoms s and t . (We have put all the β 's equal only for the sake of clarity.)

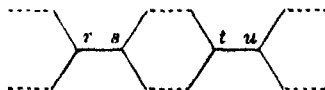


FIGURE 1

Now suppose that the values of l for the different routes all have the same residue (modulo 4). Then, since $-\beta$ is a positive quantity, it follows from (2) that

$$\left. \begin{aligned} (-)^{r+t}\Delta_{r,t}(iy)/\Delta(iy) & \text{ is of the form } -Q, -iyQ, Q \text{ or } iyQ, \\ (-)^{s+u}\Delta_{s,u}(iy)/\Delta(iy) & \text{ is of the form } -Q, -iyQ, Q \text{ or } iyQ, \\ (-)^{r+u}\Delta_{r,u}(iy)/\Delta(iy) & \text{ is of the form } -iyQ, Q, iyQ \text{ or } -Q, \\ (-)^{s+t}\Delta_{s,t}(iy)/\Delta(iy) & \text{ is of the form } iyQ, -Q, -iyQ \text{ or } Q, \end{aligned} \right\} \quad (4)$$

according as the numbers l have residues 0, 1, 2 or 3 (modulo 4). Therefore

$$(-)^{r+s+t+u} \frac{1}{\pi} \left\{ \frac{\Delta_{r,t}\Delta_{s,u} + \Delta_{r,u}\Delta_{s,t}}{\Delta^2} \right\} (iy)$$

is of the form $Q, -Q, Q$ or $-Q$ according as this residue is 0, 1, 2 or 3. (5)

$$\text{But by I (61)} \quad \pi_{rs,tu} = \frac{(-1)^{r+s+t+u}}{\pi} \int \frac{\Delta_{r,t}\Delta_{s,u} + \Delta_{r,u}\Delta_{s,t}}{\Delta^2} dy,$$

where the determinants under the integral sign are functions of iy and the limits of integration are $\pm\infty$. It follows that if in an alternant hydrocarbon the numbers of bonds along all the routes between s and t have the same residue (modulo 4), then $\pi_{rs,tu}$ is positive or negative according as this residue is even or odd. (6)

The most important application of this result is to alternant hydrocarbons such as the diphenyl-polyenes, which contain linear chains of unsaturated carbon atoms. The mutual polarizability of two bonds in such a chain must be positive or negative according as they are separated by an even or odd number of other bonds, regardless of what unsaturated hydrocarbon groups are attached to the ends of the chain.

Another application is to the *o*- and *p*-triphenyls (see figure 2), where by (6) the mutual polarizability of bonds a and b must be negative. But (6) cannot be applied to *m*-triphenyl, since one route between a and b traverses four other bonds, and the other two, and these two numbers have different residues (modulo 4).

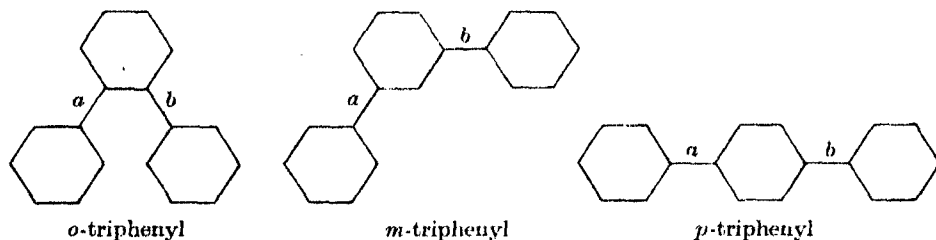


FIGURE 2

NUMERICAL VALUES OF MUTUAL BOND POLARIZABILITIES (M.B.P.)

In calculating numerical values for m.b.p.'s in unsaturated hydrocarbons, as in calculating bond orders, we assume all the carbon-carbon resonance integrals equal, with a value β say. It is then possible to calculate both the orbital energies, as multiples of β , and also the coefficients c_{rj} , which do not depend on the value of β .

But it must be recognized that in molecules where there is a great disparity between the various bond lengths, the numerical results obtained below are liable to a certain error. This is not because the formulae (e.g. equation (8)) are themselves invalid—they are not, since, for example, (8) holds even if the resonance integrals are not all equal—but because in practice we nearly always make our calculations of the coefficients c_{rj} under the assumption that every $\beta_{rs} = \beta$. For aromatic and condensed systems generally the errors in such an assumption are likely to be very small; but for butadiene (see later) they may be appreciable.

Now by equation I (19)
$$p_{rs} = 2 \sum_{j=1}^{in} c_{rj} c_{sj}, \quad (7)$$

and by II (10), for an alternant hydrocarbon

$$\pi_{rs,tu} = 4 \sum_{j=1}^{in} \sum_{\substack{k=1 \\ j < k}}^{in} \frac{(c_{rj} c_{sk} - c_{sj} c_{rk})(c_{tj} c_{uk} - c_{uj} c_{tk})}{\epsilon_j + \epsilon_k}. \quad (8)$$

From these equations and a knowledge of the structure of the molecule one can therefore calculate mobile bond orders directly, and m.b.p.'s as multiples of $1/\beta$. The results of such calculations for some important hydrocarbons are given below:

Benzene. The bond orders are all $\frac{2}{3}$, and the m.b.p.'s are:

$$\pi_{12,13} = \frac{13}{54\beta}, \quad \pi_{12,23} = \frac{-11}{54\beta}, \quad \pi_{12,34} = \frac{7}{54\beta}, \quad \pi_{12,45} = \frac{-5}{54\beta}.$$

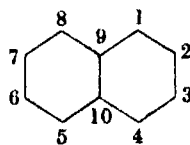


FIGURE 3

Naphthalene (see figure 3). The mobile bond orders are:

$$p_{12} = 0.725, \quad p_{23} = 0.603, \quad p_{19} = 0.555, \quad p_{9,10} = 0.518.$$

The m.b.p.'s may be found from table 1 by multiplying the figures given by $1/\beta$. The column headings give one bond and the row headings the other.

TABLE 1

	10-9	9-1	1-2	2-3
10- 9	0.253	-0.109	0.066	-0.041
9- 1	-0.109	0.288	-0.191	0.111
1- 2	0.066	-0.191	0.209	-0.209
2- 3	-0.042	0.111	-0.209	0.295
3- 4	0.066	-0.074	0.124	-0.209
4-10	-0.109	0.096	-0.074	0.111
10- 5	-0.109	-0.026	0.025	-0.045
5- 6	0.066	0.025	-0.020	0.032
6- 7	-0.042	-0.045	0.032	-0.032
7- 8	0.066	0.059	-0.032	0.032
8- 9	-0.109	-0.195	0.059	-0.045

It is interesting to observe first, that the m.b.p.'s involving a given bond alternate in sign as we move away from the bond, and secondly, that the interactions between bonds in different rings are not as small as might have been expected by analogy with mutual atom polarizabilities.

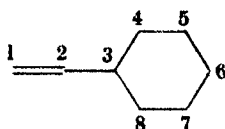


FIGURE 4

Styrene (see figure 4). The mobile bond orders in styrene are:

$$p_{12} = 0.911, \quad p_{23} = 0.406, \quad p_{34} = 0.610, \quad p_{45} = 0.679, \quad p_{56} = 0.659.$$

Values of $\beta \times \pi_{rs,tu}$ are given in table 2.

TABLE 2

	1-2	2-3	3-4	4-5	5-6
1-2	0.073	-0.155	0.044	-0.011	0.009
2-3	-0.155	0.338	-0.099	0.021	-0.014
3-4	0.044	-0.099	0.249	-0.190	0.123
4-5	-0.011	0.021	-0.190	0.247	-0.214
5-6	0.009	-0.014	0.123	-0.214	0.253
6-7	0.009	-0.014	-0.081	0.127	-0.202
7-8	-0.011	0.021	0.112	-0.091	0.127
8-3	0.044	-0.099	-0.157	0.112	-0.081

Here the m.b.p.'s of bonds in the ring are close to those in benzene. Also, it will be observed that the self-polarizability of a bond is smaller the nearer the mobile order lies to unity.

The polyenes (general formula $\text{CH}_2(\text{CH})_{n-2}\text{CH}_2$). Coulson showed that the secular equations are satisfied by

$$e_j = 2\beta \cos \frac{j\pi}{n+1}, \quad (9)$$

$$c_{rj} = \sqrt{\left(\frac{2}{n+1}\right)} \sin \frac{rj\pi}{n+1} \quad (10)$$

and that when n is even the bond orders are given by

$$p_{r,r+1} = 2 \sum_{j=1}^{\frac{1}{2}n} c_{rj} c_{r+1,j} = \frac{1}{n+1} \left\{ \operatorname{cosec} \frac{\pi}{2n+2} + (-)^{r-1} \operatorname{cosec} \frac{(2r+1)\pi}{2n+2} \right\}. \quad (11)$$

Coulson did not discuss the case of n odd. In such molecules the unpaired electron makes no contribution to the bond orders, and so

$$p_{r,r+1} = 2 \sum_{j=1}^{\frac{1}{2}(n-1)} c_{rj} c_{r+1,j} = \frac{1}{n+1} \left\{ \cot \frac{\pi}{2n+2} + (-)^{r-1} \cot \frac{(2r+1)\pi}{2n+2} \right\}. \quad (12)$$

Both the right-hand side of (11) and that of (12) are unaltered when we write $n - r + 1$ for r ; hence the bond orders are symmetric about the central atom or bond in the chain. The mobile bond orders are alternately greater and less than

$$\frac{1}{n+1} \cot (\text{or cosec}) \frac{\pi}{2n+2}$$

in each half of the chain, the differences being smaller near the middle; and the mobile order of a bond near the middle of a long polyene chain is approximately $2/\pi$, whether n is even or odd.

By equation (61) of I, the mutual polarizability of a pair of bonds in a polyene is

$$\pi_{rs,tu} = (-)^{r+s+t+u} \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Delta_{r,t} \Delta_{s,u} + \Delta_{r,u} \Delta_{s,t}}{\Delta^2} (iy) dy. \quad (13)$$

For two bonds in a chain this must be positive or negative according as the bonds rs and tu are separated by an odd or even number of bonds, as proved in (6) above.

In the notation of II, therefore, the mutual polarizability of two bonds $r, r+1$ and $t, t+1$ in a polyene chain ($r < t$) is:

$$\begin{aligned} \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\beta^{t-r} D_{r-1} D_{n-t} \beta^{t-r} D_r D_{n-t-1} + \beta^{t-r+1} D_{r-1} D_{n-t-1} \beta^{t-r-1} D_r D_{n-t}}{(D_n)^2} dy \\ = \frac{2\beta^{2t-2r}}{\pi} \int_{-\infty}^{\infty} \frac{D_r D_{r-1} D_{n-t} D_{n-t-1}}{(D_n)^2} dy, \end{aligned} \quad (14)$$

where each D is taken as a function of iy . By similar reasoning to that used in II this may be proved equal to

$$\frac{4i}{\beta\pi} \int_0^t \frac{z^{2(t-r)} (z^{2r} - 1) (z^{2r+2} - 1) (z^{2n-2t} - 1) (z^{2n-2t+2} - 1)}{(z^{2n+2} - 1)^2 (z^2 - 1)} dz. \quad (15)$$

This expression may be simplified in special cases, e.g.:

(a) For two bonds in the middle of a long polyene chain, n, r and $n-t$ are all large; therefore

$$\pi_{r,r+1;t,t+1} \simeq \frac{4i}{\beta\pi} \int_0^t \frac{z^{2t-2r} dz}{z^2 - 1}. \quad (16)$$

This takes the values $-0.273, 0.151, -0.104, 0.078, \dots, \times 1/\beta$ when $t-r$ equals $1, 2, 3, 4, \dots$

(b) For two bonds in a long polyene chain, when one bond is at the end of the chain, the mutual polarizability is

$$\begin{aligned} \pi_{1,2;t,t+1} &\simeq \frac{4i}{\beta\pi} \int_0^t z^{2t-2} (z^4 - 1) dz \\ &= \frac{(-)^{t-1} 16}{\beta\pi(2t-1)(2t+3)}. \end{aligned} \quad (17)$$

This takes the values $-0.25, 0.12, -0.07, \dots, \times 1/\beta$ when t equals $2, 3, 4, \dots$

Equation (14) does not hold when $t = r$, that is, for the self-polarizability of a bond in a polyene. For by equation (13)

$$\begin{aligned}\pi_{r,r+1;r,r+1} &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Delta_{r,r} \Delta_{r+1,r+1} + \Delta_{r,r+1}^2}{\Delta^2} (iy) dy \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{D_{r-1} D_{n-r} D_r D_{n-r-1} + \beta^2 D_{r-1}^2 D_{n-r-1}^2}{D_n^2} (iy) dy.\end{aligned}\quad (18)$$

This may be proved equal to

$$\begin{aligned}\frac{2i}{\beta\pi} \int_0^i \frac{(z^{2r}-1)(z^{2r+2}-1)(z^{2n-2r}-1)(z^{2n-2r+2}-1)}{(z^{2n+2}-1)^2(z^2-1)} dz \\ + \frac{2i}{\beta\pi} \int_0^i \frac{z^2(z^{2r}-1)^2(z^{2n-2r}-1)^2}{(z^{2n+2}-1)^2(z^2-1)} dz.\end{aligned}\quad (19)$$

(19) may also be simplified when n is large:

(a) For a bond in the middle of a long polyene chain, when r and $n-r$ are both large, equation (19) for the self-polarizability becomes

$$\frac{2i}{\beta\pi} \int_0^i \frac{dz}{z^2-1} + \frac{2i}{\beta\pi} \int_0^i \frac{z^2 dz}{z^2-1} = \frac{1}{\beta} \left(1 - \frac{2}{\pi}\right) = 0.363/\beta.$$

(b) For the terminal bond in a long polyene chain (19) becomes

$$\frac{2i}{\beta\pi} \int_0^i (z^4-1) dz + \frac{2i}{\beta\pi} \int_0^i z^2(z^2-1) dz = 8/15\beta\pi = 0.170/\beta.$$

Disregarding self-polarizabilities, therefore, we see that in all the above special cases the mutual polarizability of a pair of bonds in a long polyene decreases with distance, as well as alternating in sign.



FIGURE 5

Butadiene and hexatriene (see figure 5). The bond orders in butadiene are:

$$p_{12} = 0.894 = p_{34}, \quad p_{23} = 0.447;$$

and in hexatriene:

$$p_{12} = 0.871 = p_{56}, \quad p_{23} = 0.483 = p_{45}, \quad p_{34} = 0.784.$$

The m.b.p. may be found from tables 3 and 4 (the figure given is $\pi_{rs,tu} \times \beta$).

TABLE 3. BUTADIENE

	1-2	2-3	3-4
1-2	0.089	-0.179	0.089
2-3	-0.179	0.358	-0.179

TABLE 4. HEXATRIENE

	1-2	2-3	3-4	4-5	5-6
1-2	0.124	-0.211	0.097	-0.038	0.028
2-3	-0.211	0.370	-0.183	0.059	-0.038
3-4	0.097	-0.183	0.167	-0.183	0.097

Here again, therefore, as in styrene, the higher the order of a bond, the lower is its self-polarizability.

It should be remembered that all the above values of bond orders and m.b.p.'s have been calculated on the assumption that the resonance integrals of all the bonds are equal in all the molecules discussed. In part V we shall take into account variations in β , and see how this affects the calculated values of bond lengths and bond orders.

VARIATION OF BOND ORDERS WITH COULOMB TERMS

Having considered changes in bond order arising from changes in resonance integrals, which in their turn depend on bond lengths, we may now enquire how bond orders change when the Coulomb term of one or more atoms of the system is altered, as for instance in chemical substitution.

Now in an alternant hydrocarbon, by equation (21) of II, all bond-atom polarizabilities are zero; that is, a small change in the Coulomb term of atom r produces only a second-order change in the order of bond st . It would therefore be roughly true to say, for example, that the bond orders in quinoline are equal to those in naphthalene. But in fact it is possible to make more precise deductions about the bond orders in a molecule in which the Coulomb term of one atom departs considerably from zero.

Consider a molecule such as aniline, derived from an odd-numbered alternant hydrocarbon by replacement of one carbon by a hetero-atom, the total number of π -electrons being increased by one. Then for one atom (atom r , say) α will be negative, and by the result of II, p. 30, all the occupied mobile orders will have negative energies. It follows that we can apply I (42), viz.:

$$(-)^{s+t+1} p_{st} = \frac{1}{\pi} \int \frac{\Delta_{s,t}^*(iy)}{\Delta^*(iy)} dy, \quad (20)$$

where Δ^* refers to the hetero-molecule. If Δ denotes the secular determinant for the parent hydrocarbon, this may be expanded to give

$$(-)^{s+t+1} p_{st} = \frac{1}{\pi} \int \frac{\Delta_{s,t} + \alpha_r \Delta_{rs,rt}}{\Delta + \alpha_r \Delta_{r,r}} dy. \quad (21)$$

Therefore

$$(-)^{s+t+1} p_{st} = \frac{\alpha_r}{\pi} \int \frac{-\Delta_{s,t} \Delta_{r,r} + \Delta \cdot \Delta_{rs,rt}}{\Delta^2 - \alpha_r^2 \Delta_{r,r}^2} dy + \frac{1}{\pi} \int \frac{\Delta_{s,t} \Delta - \alpha_r^2 \Delta_{rs,rt} \Delta_{r,r}}{\Delta^2 - \alpha_r^2 \Delta_{r,r}^2} dy. \quad (22)$$

It follows from II, table 1, that the numerator in the first integrand in (22) is an odd function, and the denominator an even function; therefore the first integral is zero.

As for the second integral in (22), both numerator and denominator are real, and by II (5), Δ^2 and $-\alpha_r^2 \Delta_{r,r}^2$ have the same sign. Therefore the integrand lies between

$$\Delta_{s,t}(iy)/\Delta(iy) \quad \text{and} \quad \Delta_{rs,rt}(iy)/\Delta_{r,r}(iy),$$

Therefore p_{st} lies between

$$(-)^{s+t+1} \frac{1}{\pi} \int \frac{\Delta_{s,t}}{\Delta} dy \quad \text{and} \quad (-)^{s+t+1} \frac{1}{\pi} \int \frac{\Delta_{rs,rt}}{\Delta_{r,r}} dy$$

or their principal values. Therefore the mobile order of a bond in an alternant molecule with one hetero-atom has a value intermediate between its values in (a) the hydrocarbon obtained by replacement of the hetero-atom by a carbon atom, and (b) the hydrocarbon which remains when the hetero-atom is struck out. (23)

For example, the bond orders in aniline lie between those in benzyl and those in benzene. This theorem only holds if corresponding resonance integrals are equal in the hetero-molecule and the related hydrocarbons, but if this restriction is borne in mind, not only is the result useful in fixing limits for bond orders in hetero-molecules, but it also provides an alternative picture of the changes in bond order which are thought to arise from the occurrence of subsidiary resonance states. Take pyridine for instance. From the resonance standpoint, all the structures in figure 6 are supposed (e.g. Sidgwick 1937) on chemical grounds to contribute to the state of the molecule, causing, besides displacements of charge, differences in bond order from benzene: bonds *a*, and to a lesser extent bonds *c*, will have lowered orders, and bonds *b* will have slightly enhanced orders. By the mobile order theory, according to (23) the bonds in pyridine must have mobile orders intermediate between those in benzene, where complete conjugation occurs, and those in the pentadienyl radical, where there is no atomic orbital corresponding to the nitrogen atom. The actual values are given in table 5, and are seen both to conform to (23), and to differ in the direction indicated by the resonance theory.

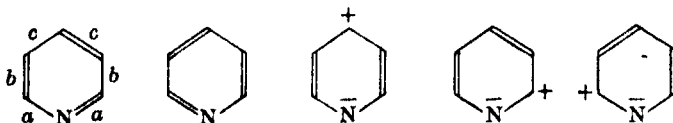


FIGURE 6. Resonance in pyridine.

TABLE 5. MOBILE BOND ORDERS IN PYRIDINE

	bonds <i>a</i>	bonds <i>b</i>	bonds <i>c</i>
benzene	0.667	0.667	0.667
pyridine	0.534	0.703	0.639
pentadienyl	0	0.789	0.577

As a final example let us consider acrolein. The electron affinity of oxygen is much greater than that of carbon, so that α for the oxygen atom in acrolein is large and negative. This causes the electron densities to be alternately large and small along the chain, as proved in II; and if the resonance integrals of all the unsaturated

bonds were equal, the bond orders in acrolein would necessarily have values intermediate between those in butadiene and those in the allyl radical, by (23). Such effects would correctly be described by the usual δ -symbols and curved arrows of the organic chemist (see figure 7 (b)), which are intended to express the difference between a molecule such as acrolein and its parent hydrocarbon butadiene (Wheland 1944). However, the resonance integral for the C=O bond is certainly much larger than that of the C=C bond, and this means that the mobile orders of the first and third bonds in acrolein will tend to be increased at the expense of the second, from what has been proved about m.b.p.'s in chain molecules. The direction of change of bond order as we pass from butadiene to acrolein is therefore governed by two conflicting effects; and numerical calculations (Coulson 1946) show that in fact the C—C bond in acrolein has a lower order than the C=C bond in butadiene. Thus although the δ -symbols describe correctly the charge distribution in acrolein, the curved arrows give a false picture of the differences in bond order between this molecule and butadiene.

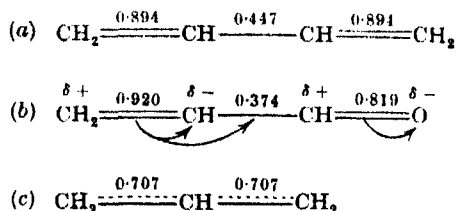


FIGURE 7

The divergence between the present semi-quantitative treatment and the qualitative resonance picture arises entirely from the fact that the resonance integral of C=O is large compared to that of C=C; however, in nitrogen compounds we should expect concordance between the two accounts, since the resonance integrals of C=C and C=N are nearly equal.

IV. Force constants and interaction constants in unsaturated hydrocarbons

In this part it is shown that the force constant of a bond in a conjugated system depends upon its 'self-polarizability' as well as upon its mobile order, and that the interaction constant between a pair of bonds is closely related to their 'mutual polarizability'. The theory is applied to benzene, where good agreement is found with the scanty evidence available, and to naphthalene and butadiene, for which at present the force constants are not known.

INTRODUCTION

In discussing the vibrational frequencies of a molecule in a given electronic level it is convenient to begin by dividing the energy of the molecule into two parts, namely $\mathcal{F}$, the kinetic energy of the nuclei, and $\mathcal{V}$, the vibrational potential energy, which

depends solely upon the configuration of the nuclei. If $q_1, q_2, \dots$ is any set of co-ordinates specifying completely the internuclear distances and angles, then $\mathcal{V}$ may be expanded as a Taylor's series about any configuration $\bar{q}_1, \bar{q}_2, \dots$ as follows:

$$\begin{aligned} \mathcal{V}(q_1, q_2, \dots) = & \mathcal{V}(\bar{q}_1, \bar{q}_2, \dots) + \sum_r \frac{\partial \mathcal{V}}{\partial q_r} (q_r - \bar{q}_r) + \frac{1}{2} \sum_r \sum_s \frac{\partial^2 \mathcal{V}}{\partial q_r \partial q_s} (q_r - \bar{q}_r) (q_s - \bar{q}_s) \\ & + \frac{1}{6} \sum_r \sum_s \sum_t \frac{\partial^3 \mathcal{V}}{\partial q_r \partial q_s \partial q_t} (q_r - \bar{q}_r) (q_s - \bar{q}_s) (q_t - \bar{q}_t) + \dots, \quad (1) \end{aligned}$$

where $\partial \mathcal{V} / \partial \bar{q}_r$ denotes the value of $\partial \mathcal{V} / \partial q_r$ in the given configuration.

Now if $\bar{q}_1, \bar{q}_2, \dots$ refer to the equilibrium configuration, then the first sum on the right vanishes; and if the displacements $q_r - \bar{q}_r$ are small, the triple sum will be negligible compared to the double sum. Under these conditions, therefore

$$\mathcal{V}(q_1, q_2, \dots) - \mathcal{V}(\bar{q}_1, \bar{q}_2, \dots) = \frac{1}{2} \sum_r \sum_s \frac{\partial^2 \mathcal{V}}{\partial q_r \partial q_s} (q_r - \bar{q}_r) (q_s - \bar{q}_s). \quad (2)$$

In general the co-ordinates q_r may be chosen in several different ways. Usually a valence-force treatment (Bjerrum 1914) is adopted; that is, the potential energy is expressed in terms of the distances x_r between bonded atoms and the angles between bonds to an atom, together with any other parameters which are needed to fix the configuration unambiguously, for instance the relative orientation of the two CH_3 groups in ethane. $\partial^2 \mathcal{V} / \partial x_r^2$ is then referred to as the force constant of the r th bond, and $\partial^2 \mathcal{V} / \partial x_r \partial x_s$ as the interaction constant of bonds r and s .*

In a valence-force treatment it often happens that the frequencies of vibration can be accounted for satisfactorily by assuming a potential function in which the interaction terms involving the product of two different co-ordinates are zero or very small. However, in many molecules it is necessary to introduce such cross terms into the potential function in order to secure agreement with observation. In a valence force potential function cross terms may obviously be of three types, representing interactions between two bonds, a bond and an angle, or two angles. A discussion of the different effects responsible for such interactions has been given by Coulson, Duchesne & Manneback (1947). However in this paper we shall be concerned exclusively with resonance interactions between pairs of bonds in a conjugated system. It will be shown that the mobile electrons in such molecules would be expected to give rise to interactions between unsaturated bonds, and that the interaction constants are closely related to the mutual bond polarizabilities (m.b.p.'s) defined in I.

* To avoid confusion it should be pointed out that in this paper the suffixes r and s in $x_r, x_s, \beta_r, \beta_s, \pi_{r,r}$ and $\pi_{r,s}$ denote bonds, not atoms. Thus $\pi_{r,s}$ stands for the mutual polarizability of the bonds r and s , whereas in papers I and II it indicated the mutual polarizability of atoms r and s , and mutual bond polarizabilities were denoted by $\pi_{r,r,\text{etc.}}$ etc. The only exception to this scheme of notation is in the relation of the theory to benzene and naphthalene, where a previously existing notation has been incorporated in our comparison with experiment.

FORM OF THE VIBRATIONAL POTENTIAL ENERGY

In order to calculate force constants and interaction terms it is necessary to make some assumptions about the dependence of $\mathcal{V}$ upon bond lengths and angles. The assumptions that we shall use will be the same as those originally introduced by Lennard-Jones (1937), and summarized by Lennard-Jones & Coulson (1939): we shall repeat their equations in this section for the sake of clearness.

For any change of configuration in the carbon skeleton of an unsaturated hydrocarbon one may formally write

$$\delta\mathcal{V} = \delta\mathcal{F} + \delta\mathcal{E}, \quad (3)$$

where $\mathcal{F}$ is the energy of the σ -bonds and $\mathcal{E}$ the total energy of the π -electrons. If we ignore changes in energy due to angular distortion, and interactions between different σ -bonds, we may follow Lennard-Jones, and put

$$\mathcal{F} = \sum_r \frac{1}{2}\sigma(x_r - s)^2, \quad (4)$$

where σ , s are the force constant and length of a pure σ -bond, and x_r is the length of the r th bond. $\mathcal{E}$, on the other hand, is most conveniently expressed as a function of the resonance integrals of the unsaturated bonds, the resonance integral β_r of the r th bond depending only on its length x_r . For this dependence Lennard-Jones assumed

$$2\beta_r = \text{const.} + \frac{1}{2}\kappa(x_r - d)^2 - \frac{1}{2}\sigma(x_r - s)^2,$$

so that

$$\frac{d\beta_r}{dx_r} = \frac{1}{2}\kappa(x_r - d) - \frac{1}{2}\sigma(x_r - s), \quad (5)$$

where κ , d are the force constant and length of a pure double bond. (σ and κ in our notation stand for $2\kappa_s$ and $2\kappa_d$ in the notation of Lennard-Jones & Coulson.)

BOND LENGTHS IN EQUILIBRIUM

The conditions that the bond lengths shall have their equilibrium values $\bar{x}_r$ are that

$$\frac{\partial\mathcal{V}}{\partial x_r} = 0 \quad \text{for each bond.}$$

But by (3)

$$\frac{\partial\mathcal{V}}{\partial x_r} = \frac{\partial\mathcal{F}}{\partial x_r} + \frac{d\beta_r}{dx_r} \frac{\partial\mathcal{E}}{\partial\beta_r}, \quad (6)$$

and by I (25),

$$\frac{\partial\mathcal{E}}{\partial\beta_r} = 2p_r,$$

where p_r is the mobile order of bond r . It follows from (4) and (5) that the equilibrium bond lengths $\bar{x}_r$ are given by

$$\sigma(\bar{x}_r - s) + p_r\{\kappa(\bar{x}_r - d) - \sigma(\bar{x}_r - s)\} = 0,$$

whence

$$\bar{x}_r = \frac{d\kappa p_r + s\sigma(1 - p_r)}{\kappa p_r + \sigma(1 - p_r)}. \quad (7)$$

This could be written (see Coulson 1939)

$$x_r = s - \frac{s-d}{1 + \frac{\sigma}{\kappa} \left(\frac{1-p_r}{p_r} \right)},$$

and suggests that in quite general form, the relation between mobile order p and length x should be

$$x = A + \frac{B}{1 + C \left(\frac{1-p}{p} \right)}, \quad (8)$$

where A , B and C are constants which will have different values for each type of bond, e.g. C—C, C—O, C—N. In view of the theoretical basis for such a formula as (8), and its satisfactory agreement with experiment, there does not seem to be any great advantage to be gained from introducing other entirely empirical relationships between x and p , as has recently been proposed (Kavanau 1944; Lagermann 1946; Bernstein 1947; Gordy 1947).

FORCE CONSTANTS AND INTERACTION TERMS

By equation (3) the force constant of bond r satisfies the equation

$$\frac{\partial^2 \mathcal{V}}{\partial \bar{x}_r^2} = \frac{\partial^2 \mathcal{F}}{\partial \bar{x}_r^2} + \frac{\partial^2 \mathcal{G}}{\partial \bar{x}_r^2}.$$

But $\mathcal{G}$ is a function of the β 's, and each β is a function of the corresponding bond length; therefore the right-hand side becomes

$$\frac{\partial^2 \mathcal{F}}{\partial \bar{x}_r^2} + \frac{d^2 \beta_r}{d \bar{x}_r^2} \frac{\partial \mathcal{G}}{\partial \beta_r} + \left(\frac{d \beta_r}{d \bar{x}_r} \right)^2 \frac{\partial^2 \mathcal{G}}{\partial \beta_r^2} = \sigma + (\kappa - \sigma) p_r + \left\{ \frac{1}{2} \kappa (\bar{x}_r - d) - \frac{1}{2} \sigma (\bar{x}_r - s) \right\}^2 2 \pi_{r,r},$$

where $\pi_{r,r}$ is the self-polarizability of the r th bond (see I). Substitution for $\bar{x}_r$ from (7) gives

$$\frac{\partial^2 \mathcal{V}}{\partial \bar{x}_r^2} = \sigma(1-p_r) + \kappa p_r + \frac{1}{2} \left\{ \frac{\kappa \sigma (s-d)}{\sigma(1-p_r) + \kappa p_r} \right\}^2 \pi_{r,r}. \quad (9)$$

Similarly, the interaction constant of bonds r and s is given by

$$\frac{\partial^2 \mathcal{V}}{\partial \bar{x}_r \partial \bar{x}_s} = \frac{\partial^2 \mathcal{F}}{\partial \bar{x}_r \partial \bar{x}_s} + \frac{\partial^2 \mathcal{G}}{\partial \bar{x}_r \partial \bar{x}_s} = \frac{d \beta_r}{d \bar{x}_r} \frac{d \beta_s}{d \bar{x}_s} \frac{\partial^2 \mathcal{G}}{\partial \beta_r \partial \beta_s} = \frac{1}{2} \left\{ \frac{\kappa \sigma (s-d)}{\sigma(1-p_r) + \kappa p_r} \right\} \left\{ \frac{\kappa \sigma (s-d)}{\sigma(1-p_s) + \kappa p_s} \right\} \pi_{r,s}, \quad (10)$$

where $\pi_{r,s}$ is the mutual polarizability of bonds r and s . Equations (9) and (10) may be more simply written

$$\frac{\partial^2 \mathcal{V}}{\partial \bar{x}_r^2} = \lambda_r + \frac{\mu \pi_{r,r}}{\lambda_r^2} \quad (11)$$

and

$$\frac{\partial^2 \mathcal{V}}{\partial \bar{x}_r \partial \bar{x}_s} = \frac{\mu \pi_{r,s}}{\lambda_r \lambda_s}, \quad (12)$$

where

$$\lambda_r = \sigma(1-p_r) + \kappa p_r, \quad \lambda_s = \sigma(1-p_s) + \kappa p_s \quad (13)$$

and

$$\mu = \frac{1}{2} \kappa^2 \sigma^2 (s-d)^2.$$

The above equations have an interesting physical significance. The force constant of a bond appears as the sum of two terms, the first of which is linearly related to the bond order, whereas the second term depends principally on the self-polarizability of the bond, and has the form of an interaction constant. We see therefore that (a) the force constant of a bond depends on its self-polarizability as well as on its mobile order, and (b) the interaction between two bonds is proportional to their mutual polarizability, but also depends on their mobile orders.

APPLICATION TO BENZENE

One of the simplest molecules to which equations (11) and (12) may be applied is benzene, where there is only one kind of CC bond and only three types of interaction constant between different CC bonds.

Let us number the atoms in benzene consecutively round the ring, 1 to 6. Then by III the m.b.p.'s are

$$\pi_{1-2,1-2} = \frac{13}{54\beta}, \quad \pi_{1-2,2-3} = \frac{-11}{54\beta}, \quad \pi_{1-2,3-4} = \frac{7}{54\beta}, \quad \pi_{1-2,4-5} = \frac{-5}{54\beta}, \quad (14)$$

and the mobile order of every bond is $2/3$.

In what follows we shall use the notation of Manneback (1935) for the force constants in benzene. He writes

$$\frac{\partial^2 \psi}{\partial \bar{x}_{1-2}^2} = F, \quad \frac{\partial^2 \psi}{\partial \bar{x}_{1-2} \partial \bar{x}_{2-3}} = F_0, \quad \frac{\partial^2 \psi}{\partial \bar{x}_{1-2} \partial \bar{x}_{3-4}} = F_m, \quad \frac{\partial^2 \psi}{\partial \bar{x}_{1-2} \partial \bar{x}_{4-5}} = F_p.$$

In calculating F , F_0 , F_m and F_p we substitute into equations (9) and (10) the following experimentally determined values:

$$s = 1.54 \text{ \AA}, \quad \sigma = 4.96 \times 10^5 \text{ dyne/cm.}, \\ d = 1.33 \text{ \AA}, \quad \kappa = 9.80 \times 10^5 \text{ dyne/cm.},$$

these figures being those used by Lennard-Jones & Coulson, and

$$\beta = -20 \text{ Cal./mole} = -1.39 \times 10^{-12} \text{ erg},$$

from measured resonance energies (Wheland 1941). The results are:

$$F = 6.84, \quad F_0 = 1.14, \quad F_m = -0.73, \quad F_p = 0.52 \times 10^5 \text{ dyne/cm.}$$

These figures may be compared with those given by Duchesne & Penney (1939) on the basis of the vibrational spectrum of benzene, viz.:

$$F - F_0 - F_m + F_p = 5.78 \quad (\text{calc. } 6.95) \times 10^5 \text{ dyne/cm.} \\ F + 2F_0 + 2F_m + F_p = 7.57 \quad (\text{calc. } 8.19) \times 10^5 \text{ dyne/cm.}$$

and, with certain auxiliary assumptions, including that $F_p = 0$,

$$F + F_0 - F_m - F_p = 7.50 \quad (\text{calc. } 8.19) \times 10^5 \text{ dyne/cm.} \\ F - 2F_0 + 2F_m - F_p = 4.33 \quad (\text{calc. } 2.58) \times 10^5 \text{ dyne/cm.}$$

Although the data are scanty, agreement is fair, particularly as there is considerable uncertainty as to what values should be taken for s , d , σ , κ and β . Fortunately, however, we have been able to show, by taking somewhat altered numerical values for some of these quantities, that even if different values were chosen, the calculated cross-terms would still be of the right order of magnitude. In the last force constant the discrepancy may be partly due to the inaccuracy of the secondary assumptions made by Duchesne & Penney in evaluating the empirical cross-terms; in particular, it cannot be correct to assume that $F_p = 0$. A better assumption would be that $F_0:F_m:F_p = -11:7:-5$ as suggested theoretically by (12) and (14). It is worth noting that whatever values are taken for σ , κ , s and d , the effective force constants $F + F_0 - F_m - F_p$ and $F + 2F_0 + 2F_m + F_p$ must be equal since both reduce to $\kappa p + \sigma(1-p)$ owing to the relative values of the m.b.p.'s in benzene; and this is confirmed by the empirical results, within experimental error, for the two values are 7.50 and 7.57×10^5 dyne/cm, respectively.

While the assumptions of the present theory seem to be more or less valid for benzene, it should be realized that benzene is a particularly favourable test case, for the following reasons:

(a) In calculating bond orders and mutual bond polarizabilities—and hence force constants and interaction terms—it is necessary to assume the resonance integrals of all the unsaturated bonds equal, in order to avoid unmanageable mathematical complexities. Almost the only hydrocarbon for which this is true is benzene, since in other molecules the unsaturated bonds will differ in mobile order and therefore in length and resonance integral.

(b) In deriving equations (11) to (13) we have neglected changes in bond angle, and in five of the planar vibrations of benzene the ring angles are unchanged.

(c) Equation (5), which implies a parabolic variation of β with bond length, will probably not hold over a wide range of x , but this does not matter in benzene, since even when the molecule is vibrating the differences between the bond lengths are small.

APPLICATION TO NAPHTHALENE

In view of the structural similarity between benzene and naphthalene, one might expect the approximations of the present theory to be almost equally valid for both molecules; and since at present no experimental values of CC force constants or interaction terms are available for naphthalene, this molecule affords an instance in which the quantitative predictions of the theory may be verified *a posteriori*.

It is most convenient to consider separately the potential functions for the different symmetry classes. As we are concerned with changes in bond length, the only symmetry classes we need consider are those in which the plane of the molecule is a plane of symmetry, viz. A_{1g} , B_{1g} , B_{2u} and B_{3u} .* If we use the conventional numbering for the atoms in naphthalene, and denote the changes in bond length during

* The notation is that of Herzberg (1945, p. 108), where the z -axis, called 1, is perpendicular to the molecular plane, and the y -axis, called 2, lies along the common bond of the two rings.

a vibration by Δx_{1-2} , etc., then the following relations hold in the above symmetry classes:

$$A_{1g} \quad \Delta x_{9-10} = a, \text{ say.}$$

$$\Delta x_{9-1} = \Delta x_{9-8} = \Delta x_{10-4} = \Delta x_{10-5} = b, \text{ say,}$$

$$\Delta x_{1-2} = \Delta x_{3-4} = \Delta x_{5-6} = \Delta x_{7-8} = c, \text{ say,}$$

$$\Delta x_{2-3} = \Delta x_{6-7} = d, \text{ say.}$$

$$B_{1g} \quad \Delta x_{9-10} = 0,$$

$$\Delta x_{9-1} = -\Delta x_{9-8} = -\Delta x_{10-4} = \Delta x_{10-5} = b, \text{ say,}$$

$$\Delta x_{1-2} = -\Delta x_{3-4} = \Delta x_{5-6} = -\Delta x_{7-8} = c, \text{ say,}$$

$$\Delta x_{2-3} = \Delta x_{6-7} = 0.$$

$$B_{2u} \quad \Delta x_{9-10} = 0,$$

$$\Delta x_{9-1} = \Delta x_{9-8} = -\Delta x_{10-4} = -\Delta x_{10-5} = b, \text{ say,}$$

$$\Delta x_{1-2} = -\Delta x_{3-4} = -\Delta x_{5-6} = \Delta x_{7-8} = c, \text{ say,}$$

$$\Delta x_{2-3} = \Delta x_{6-7} = 0.$$

$$B_{3u} \quad \Delta x_{9-10} = 0,$$

$$\Delta x_{9-1} = -\Delta x_{9-8} = \Delta x_{10-4} = -\Delta x_{10-5} = b, \text{ say,}$$

$$\Delta x_{1-2} = \Delta x_{3-4} = -\Delta x_{5-6} = -\Delta x_{7-8} = c, \text{ say,}$$

$$\Delta x_{2-3} = -\Delta x_{6-7} = d, \text{ say.}$$

If the potential energy $\mathcal{V}$ in (2) is now expanded in terms of a , b , c and d , a similar calculation to that for benzene gives the following effective force constants and interaction terms:

	A_{1g}	B_{1g}	B_{2u}	B_{3u}
$\partial^2 \mathcal{V} / \partial a^2$	5.8	—	—	—
$\partial^2 \mathcal{V} / \partial a \partial b$	2.9	—	—	—
$\partial^2 \mathcal{V} / \partial a \partial c$	-1.6	—	—	—
$\partial^2 \mathcal{V} / \partial a \partial d$	0.53	—	—	—
$\partial^2 \mathcal{V} / \partial b^2$	25	23	29	16
$\partial^2 \mathcal{V} / \partial b \partial c$	4.0	3.3	1.7	7.9
$\partial^2 \mathcal{V} / \partial b \partial d$	-1.7	—	—	-3.9
$\partial^2 \mathcal{V} / \partial c^2$	28	32	32	26
$\partial^2 \mathcal{V} / \partial c \partial d$	4.0	—	—	5.4
$\partial^2 \mathcal{V} / \partial d^2$	13	—	—	12

Effective force constants and interaction constants in naphthalene (units of 10^4 dyne/cm.)

Although the parameters used in the calculations were the same as those used for benzene, the figures above would probably not be greatly affected if the parameters were assigned slightly different values.

Attention is drawn to the signs of the interaction constants, no less than three of which are negative; and to their high values in the vibrations of species B_{3u} . This table also shows how dangerous it is to speak of 'the force constant for a bond'. If, for example, there were no interaction between the bonds 9-1, 9-8, 10-4 and

10-5, all four entries in the row labelled $\partial^2\mathcal{V}/\partial b^2$ would be equal, although the letter b represents different normal co-ordinates in the different symmetry classes. In fact, $\partial^2\mathcal{V}/\partial b^2$ varies over almost a factor of two. There is a close parallel here to some work (Thorndike, Wells & Wilson 1947) on the intensities of infra-red absorption where, for example, it is shown from a careful analysis of experimental observation that the dipole moment of C—H in ethylene has effective values that range from 0.37 to 0.77 Debyes according to the type of vibration that is being excited. We are forced to the conclusion that, particularly in conjugated systems, neither the dipole moment nor the vibrational potential energy of a molecule are sums of contributions from the separate lengths and angles, but that both quantities involve also significant cross terms between these co-ordinates.

It will also be noticed that the interaction terms are sometimes quite large, even up to 2/3 of the force constants. Evidently no empirical representation of the force fields of molecules of this type is likely to be found which does not include a large number of such cross-terms.

BUTADIENE

There are only two kinds of vibration involving changes in the CC bond lengths in butadiene. In the first

$$\Delta x_{1-2} = \Delta x_{3-4} = a, \text{ say} \quad \text{and} \quad \Delta x_{2-3} = b, \text{ say};$$

and in the second

$$\Delta x_{1-2} = -\Delta x_{3-4} = a, \text{ say} \quad \text{and} \quad \Delta x_{2-3} = 0.$$

Using the same parameters as in the benzene calculations, and the mutual bond polarizabilities given in III, one obtains the following constants: in the former type of vibration

$$\partial^2\mathcal{V}/\partial a^2 = 17, \quad \partial^2\mathcal{V}/\partial b^2 = 4.4, \quad \partial^2\mathcal{V}/\partial a\partial b = 2.1 \times 10^5 \text{ dyne/cm.}$$

and in the latter type $\partial^2\mathcal{V}/\partial a^2 = 18 \times 10^5 \text{ dyne/cm.}$

Although these figures are qualitatively reasonable, their actual values are probably not very reliable, for the following reasons. First, the bond orders in butadiene differ considerably, which means that it is a bad approximation to assume the resonance integrals equal in calculating bond orders and m.b.p.'s. Secondly, equations (4) and (5) cannot be expected to hold for differences in bond length as large as those in butadiene. Finally, in view of the above uncertainties it is difficult to decide what is the best value to assume for β in evaluating the m.b.p.'s, which appear as multiples of $1/\beta$. We have therefore used the benzene value for uniformity.

CONCLUSIONS

The conclusions to be drawn from the present investigation seem to be as follows:

(i) The force constant of an unsaturated bond in a conjugated system will depend on its self-polarizability as well as on its mobile order.

(ii) A pair of unsaturated bonds in a conjugated system will in general interact, the interaction constant being proportional to the mutual polarizability of the bonds, but also involving their mobile orders.

(iii) Owing to the nature of the approximations occurring in the theory, one would expect the equations to hold most exactly for molecules in which there is not much variation in mobile order between the bonds; indeed, the theory is in moderately good agreement with the experimental data for benzene.

(iv) The theory takes no account of interactions between σ -bonds. The fact that in many saturated molecules (e.g. CCl_4) the observed frequencies of vibration imply considerable cross-terms in the potential function (Herzberg 1945) means that this will not in general be a valid approximation; in fact, preliminary work (unpublished) on the chloroethylenes indicates that the present theory is not general enough to account for their potential functions. But this does not seem to apply to hydrocarbons; for instance, in CH_4 , a simple valence-force potential function without cross-terms gives a satisfactory interpretation of the vibrational spectrum.

To sum up, although the present theory takes no account of angular strain or σ -bond interactions, its comparative success when applied to benzene suggests that in unsaturated hydrocarbons the interactions between the unsaturated bonds arise primarily from the mobile electrons.

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The thermal etching of silver

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[PLATES 9 TO 12]

The mechanism whereby grain boundaries are delineated and striations formed on polished surfaces of heated metal specimens has been examined. Experiments on electrolytically polished silver show that grooves form at grain boundaries at temperatures as low as 300° C and striations at 500° C in air. Striations only appear in the presence of oxygen and may be removed by heating in nitrogen.

A furnace for high-temperature photomicrography, suitable for specimen temperatures up to about 950° C, is described.

Previous theories are found inadequate to explain the effects observed in silver, and a theory which regards the surface etching as an approach to equilibrium by the reduction of surface free energy is suggested. Thus the equilibrium condition of the boundary is a groove whose shape is determined by the relative magnitudes of the free energy per unit area of the boundary and the surface energies of the crystalline faces meeting the boundary in the surface of the specimen. The striations are caused by the development of those crystalline planes having the lowest free energy; the relative surface energies of different planes being modified by the presence of oxygen. It is suggested that the chief means whereby the boundary grooves are formed is that of surface migration of ions: both surface migration of ions and evaporation of silver oxide molecules may be expected to play major parts in the formation of the striations.

1. INTRODUCTION

The nature and the properties of the material constituting the boundaries of the crystal grains in polycrystalline metals are of profound importance in the study of metals, yet there exists comparatively little detailed information concerning them. As part of a general investigation of the grain boundary, experiments were carried out to examine the nature of the etching effect known to occur frequently on polished surfaces of metals when they are heated. When conditions are such that this etching occurs, the grain boundaries are delineated and it was felt that an understanding of the mechanism of this phenomenon would provide valuable information concerning their nature. Under some conditions of heating, polished surfaces show, besides grain-boundary markings, striations which cross the different crystal grains in different directions. As, in the course of the experiments on the grain-boundary etching, the opportunity arose to observe this effect as well, it was examined and some additional experiments designed specifically to provide information concerning it were performed.

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The experiments were all carried out on silver and it was found that none of the explanations previously put forward for the thermal-etching process was completely satisfactory for the results obtained. A tentative explanation consistent with published results is suggested.

2. PREVIOUS OBSERVATIONS UPON THERMAL ETCHING*

At the outset it is necessary to distinguish clearly between the phenomena of thermal etching and those of 'thermal fatigue' recently described by Boas & Honeycombe (1946, 1947). There are distinct similarities between the appearance of specimens which have been subjected to 'thermal fatigue' and that of specimens thermally etched. In both cases the grain boundaries are delineated upon what was initially a polished surface, and striations develop which run across the grains themselves. Despite the similarity in appearance of the specimens, however, there is little doubt that the phenomena are different. The phenomena of thermal fatigue were produced in Boas & Honeycombe's experiments by subjecting specimens of the non-cubic metals, tin, zinc and cadmium to cycles of heating and cooling, and were not observed when specimens of lead, which is cubic, were similarly treated. Boas & Honeycombe explained their results by the fact that the non-cubic metals expand and contract anisotropically when heated and cooled and thus in a randomly orientated aggregate of crystal grains stresses are set up with change of temperature. These stresses are sufficient to cause slip in certain crystals and the striations observed are in fact slip lines. The stresses also cause changes in level between different grains and the grain boundaries are delineated. With increasing numbers of cycles of heating and cooling the striations become more numerous and if grain growth occurs, there are formed, in addition to the old grain-boundary outlines, new lines which coincide with the new grain boundaries. In this way a series of boundary networks is formed, one corresponding to each cycle. The phenomena observed appeared to be independent of the environment in which the cyclic heating took place.

Boas & Honeycombe give much additional evidence in support of their explanation and 'thermal fatigue' is undoubtedly the explanation of the delineation of the grain boundaries observed by Carpenter & Elam (1920) when they heated and cooled specimens of an antimony-tin alloy.

As distinct from 'thermal fatigue' the phenomena of thermal etching are observed in many cubic metals, they can be produced by maintaining the metal at an elevated temperature without any cyclic heating and cooling, and they are affected by the environment in which the metal is heated. The grain boundaries are delineated not by difference in level between adjacent grains but by grooves formed at the intersection of the boundary with the surface. The striations are corrugations or a stepped structure of the surface.

* [Note added in proof.] Previous observations upon thermal etching have recently been reviewed; Shuttleworth, R., July, 1948, *Metallurgia*. (In course of publication.)

During the past thirty years thermal etching phenomena have been observed by numerous workers. Networks of grooves were observed on iron heated in a vacuum by Rosenhain & Humfrey (1910) and on iron heated in hydrogen by Rawdon & Berglund (1928) who also observed striations. Grain-boundary networks on steels were observed by Kroll (1912), Humfrey (1912), Rawdon & Scott (1922) and Hemingway & Ensminger (1922). The phenomenon has been used (Day & Austin 1940; Miller & Day 1942) for the determination of austenitic grain size. Parker & Smoluchowski (1945) observed that molten silver spread along the boundary grooves on a molybdenum steel more rapidly than across the crystal faces. Where explanations of the phenomena were offered they were attributed to selective evaporation.

Striations were observed on the surfaces of cast specimens by Ewing & Rosenhain (1900) and Graf (1942).

Specific attention has, however, been directed by few workers towards the understanding of the phenomena. The formation of the boundary grooves was considered by Rosenhain & Ewen (1912), who heated polished specimens of copper, silver and zinc in a vacuum and found that grooves developed at grain boundaries but not at twin boundaries. They observed that when heated under otherwise identical conditions, specimens with small grain size evaporated more rapidly than those with large grain size. They interpreted their experiments by supposing that metallic grains are joined by a cement of amorphous metal which has a greater vapour pressure than the crystalline metal. On heating in vacuum the amorphous metal exposed at the boundaries evaporates more rapidly than the grains, thus producing the boundary grooves. They attributed the greater loss of weight from the small grained specimens to the fact that they exposed more grain boundary material than did the specimens of large grain size, and also as the grooves formed the effective area was increased.

They also suggested that the grooves at the boundaries could have been produced in part by the rearrangement of the mechanically polished surface layer to conform with the crystalline structure beneath.

Fonda (1923), working on the rate of evaporation of tungsten filaments at 2677° C, found that grooves developed at the grain boundaries both in inert atmospheres and in a vacuum. In a vacuum the rate of evaporation from filaments with small grain size was 1.4 times that from filaments whose grains were 4 to 100 times longer, and Fonda attributed the phenomena he observed to the greater volatility of the grain boundary material.

Cases of the formation of striations were examined by Johnson (1938) and Gwathmey & Benton (1940*a, b*, 1942) who explained their formation by the migration of ions or the rearrangement of atoms and by Leroux & Raub (1930) and Elam (1936) who ascribed the phenomena they observed to oxidation of the surface.

Johnson (1938) observed striations on tungsten filaments, the surfaces of which he examined in considerable detail, after they had been heated under various conditions. He found that the surface structure produced by the heating depended upon the nature of the atmosphere and the heating current. Thermal gradients in

the filaments modified the surface structure. Stepped structures which occurred with D.C. heating, and were also caused by temperature gradients, Johnson supposed were produced by the surface migration of positive tungsten ions in the electric and thermal fields, the rate of drift depending upon the crystallographic direction. A subsidiary experiment showed that thorium migrated over the surface of tungsten in an ionic form, the direction of migration being influenced by an applied electric field. Johnson also found that tantalum, molybdenum, platinum, iron and nickel filaments roughened when heated with d.c. Mrowca (1943) observed very similar results on tantalum ribbons; striations appeared with d.c. heating and when there were thermal gradients. He explained the striations in the same way as Johnson.

Gwathmey & Benton (1940a, b, 1942), examining the reaction of gases on the surface of copper, used a spherical single crystal of copper whose surface was obtained unoxidized in a strain-free condition by electrolytic polishing followed by annealing in hydrogen. They found that heating in a vacuum of 10^{-4} mm., or in hydrogen at atmospheric pressure, caused no change on the surface of the crystal, but if the sphere was heated in air at pressures and temperatures which produced only a thin oxide film, an oxide pattern was produced which indicated that different crystallographic planes are oxidized at different rates. A sphere heated to $1,000^{\circ}\text{C}$ at a pressure of 0.3 mm. showed, beside this differential oxidation, circular striations spreading out to 3 to 5 mm. diameter around the (110) and (111) poles of the crystal. The striations were caused by the development of {110} and {111} planes at these positions. When the sphere was heated to 580°C in hydrogen the oxide film disappeared and the striations were diminished.

From these experiments Gwathmey & Benton concluded that at temperatures below the melting point rearrangements of the surface atoms can occur to produce facets with simple crystallographic indices.

Leroux & Raub (1930) carried out careful weighing experiments upon specimens of silver heated to temperatures of 600 and 750°C in a stream of oxygen and in a stream of air, and observed that there was a loss of weight which they attributed to the formation of an oxide which they suggested was Ag_2O , and which was volatile at the temperatures of their experiments. Striations were formed on the surface of the specimens. When the specimens were heated under similar conditions in hydrogen there was no measurable loss in weight and no striations were formed. They concluded, therefore, that the rate of oxidation was different for different crystallographic planes of the silver and that the striations were due to the development of these planes. Graf (1942) correlated the striated structure to that observed when metals solidified from the molten state.

Elam (1936) heated a mechanically polished specimen of copper containing cuprous oxide, in a vacuum of about 0.5 mm., to a temperature between 900 and 950°C , and found that striations appeared; oxygen-free copper heated under similar conditions developed no striations. If, however, the surface of the oxygen-free copper was first oxidized and the specimen then heated in a vacuum to 900°C the oxide disappeared to leave a striated surface. There was a nett loss of weight

indicating evaporation of the oxide in a molecular form. It was found that the formation of striations was very sensitive to surface preparation, and even prolonged heating at 950° C did not remove the effects of the mechanical polish.

Elam found that if an etched face was polished and reheated, the striations reappeared in the same directions and that their spacing was the same. Separate specimens cut from the same single crystal also showed the same striations on corresponding faces. Where striations appeared on three faces of a single crystal they could not be identified as the intersection of a single plane with those three surfaces, although the directions of the lines on single faces were consistent with their being the intersection of {100} or {110} planes with that surface.

The mechanism suggested by Elam for the formation of the striations is that when the surface of copper is oxidized the rate of oxidation is greatest for the {100} and the {110} planes. When the specimen is then heated in a vacuum to a high temperature, the oxide evaporates leaving a striated surface. In the case of the copper containing cuprous oxide, the oxide decomposes on heating and the oxygen diffuses to the surface, which it oxidizes. The striations are then produced as in the case of the specimen whose surface was initially oxidized.

3. EXPERIMENTAL PROCEDURE

A number of experiments were performed to examine the thermal etching of high purity silver. Preliminary experiments indicated that the phenomena were very sensitive to surface preparation, and attention was concentrated upon finding a method of preparation which gave consistent, reproducible results. A method of electrolytic polishing was found most satisfactory and a series of experiments was carried out on specimens prepared in this way to examine the effects of temperature and various atmospheres on the etching process. To examine the surface of silver specimens when they were at elevated temperatures a furnace was designed to enable microscopy to be carried out at high temperatures.

(a) Selection of material

Silver was selected as the material for the first experiments on thermal-etching phenomena for a number of reasons. Since the grain boundaries are concerned in the etching, purity of the metal is of great importance, as quite a small average impurity content might, if concentrated at the grain boundary, have a large effect. Silver may be obtained in a condition of high purity. The silver used was supplied specially by Johnson, Matthey and Co. Ltd., who cast it in a vacuum and then cold forged and cold rolled it into 8 s.w.g. sheet. Analysis showed 0.00016 % iron, 0.00014 % manganese and faint traces of magnesium, calcium, silicon and lead.

In oxygen at atmospheric pressure silver oxide (Ag_2O) in bulk is unstable and decomposes above 200° C. This reaction is reversible, but below 200° C the rate of oxidation is small, becoming negligible below 100° C (Lewis 1906; Keyes & Hara 1922; Benton & Drake 1932, 1934).

As the crystal structure of silver is cubic its thermal expansion is isotropic and no stresses are set up when a polycrystalline specimen is heated or cooled provided there are no thermal gradients in the specimen.

(b) The preparation of specimens

Initial experiments were carried out using silver which had been ground on emery papers and then mechanically polished on velvet with a commercial metal polish. Because of the softness of the silver considerable difficulty was experienced; for reasonably reproducible results a tedious process of alternately polishing and chemically etching was needed and even after this process it was found (in agreement with the results of Elam (1936) for copper) that the effects of grinding were not removed by heating to a temperature near the melting point.

Finally a method of electrolytic polishing was found, which gave reproducible results and all specimens were prepared by this process. The process is described elsewhere (Shuttleworth, King & Chalmers 1947).

(c) The effect of temperature on the etching

To examine the effect of temperature on the etching of silver, specimens were heated in a fused silica tube open to the atmosphere. The tube was placed in an electric furnace already set at the required temperature. A thermocouple placed near to the specimen was used to indicate the specimen temperature and the furnace was controlled to maintain the temperature to within $\pm 1^\circ$ C. The temperatures examined were 300, 500, 700, 850 and 940° C and figure 2, plate 9 ($\times 250$) shows the structures exhibited on examination when cool after 11 hours at these temperatures. Figure 3, plate 9 ($\times 1500$) shows the structures for 500, 850 and 940° C at a higher magnification.

Grooves have appeared at the grain boundaries and striations have occurred on the grains themselves. The striations change their direction at grain and twin boundaries. Extensive grain growth has occurred at the higher temperatures and the proportion of twinned crystals is higher at these temperatures. At 300° C no striations have appeared and the grain boundaries are incomplete. At 500° C the boundary grooves are complete and striations have begun to appear. The proportion of grains striated is seen to increase with temperature and above 850° C nearly all the grains are striated. At the higher temperatures the striations are more closely spaced and a second set of striations, inclined to the first, appear on some grains. The striations which form at the lower temperature are not as straight and regular as those formed at the higher temperature a few circular striations are shown in figure 3a ($\times 1500$). At the lower temperatures; the curvature caused by the boundary grooves appears to extend over an appreciable area of the grain surface; if the striations were the traces of specific crystallographic planes, they would be curved on a curved surface. Gwathmey & Benton (1940a, b) observed circular striations on spherical crystals of copper.

(d) The effect of atmosphere on the etching

Specimens were heated at 920° C in air, in oxygen, in pure nitrogen and in a vacuum of better than 10^{-4} mm. of mercury. The specimens were once more heated in a silica tube. The required atmosphere was established in the tube before it was placed in the furnace which was already at the required temperature. The specimen reached the required temperature in about 10 min. After the period of heating the tube was allowed to cool in air and the specimen cooled to 100° C in about 10 min. In all cases the atmosphere was maintained until the specimen cooled to room temperature.

Ordinary commercial oxygen was used and oxygen-free nitrogen. The nitrogen contained less than 10 vol./million of oxygen, less than 50 vol./million of hydrogen and less than 0.02 g./cu.m. of water vapour at 120 atm. pressure.

Typical photomicrographs of surfaces after these tests are shown in figure 4, plate 10 ($\times 250$).

In all cases extensive grain growth has occurred. In air (figure 4*a*) grain boundaries have formed and strong striations have appeared. Similar results are shown in figure 4*b* for specimens heated in oxygen, but in general the striations are more closely spaced and frequently a second set of striations appears inclined in direction to the first. In some cases a third set appears. Figure 5, plate 10 ($\times 2000$) shows the complicated structure developed in oxygen. In nitrogen, grooves appear at the grain boundaries and much less noticeably at twin boundaries; no striations appear. In a vacuum the grain boundaries show as grooves. No striations are produced, but the surface rapidly becomes rough. Figure 4*d* ($\times 250$) shows the surface after only $1\frac{1}{2}$ hr. in a vacuum at 920° C, and is therefore not strictly comparable with the other photomicrographs. It may, however, be compared with figure 8*g*, plate 12 which shows the surface after heating in air for $1\frac{1}{2}$ hr. at 920° C.

Some attempts were made at heating in hydrogen, but the results were unsatisfactory because the hydrogen was of doubtful purity. The results did, however, show no evidence of striations.

To verify that the boundary markings observed were in fact grooves as suggested by microscopic examination and not differences in level between adjacent grains, electron microscope replica photographs were obtained of a sample heated in nitrogen. The photographs confirmed that the markings were grooves below the level of both grains.

(e) The reversibility of striation etching

Because striations only appear in atmospheres containing oxygen, experiments were carried out to determine whether striations could be made to disappear by heating in nitrogen after heating in air (Shuttleworth, King & Chalmers 1946). Specimens were first heated in nitrogen until grain growth was only proceeding slowly, then in air for a sufficiently long period for striations to form, then in nitrogen for various lengths of time. Figure 6*a*, plate 11 ($\times 250$) shows the surface after 11 hr. in nitrogen at 920° C. Figure 6*b* shows the same surface after heating

for 1 hr. in air at the same temperature; striations have formed. Figures 6c, d and e show the surface after a further heating of 1, 3 and 11 hr. respectively in nitrogen; the striations have gradually disappeared. Figure 6f shows the effect of heating for a further period of 1 hr. in air. The striations have appeared in the same directions as before, but are more closely spaced.

During the preliminary anneal in nitrogen there was extensive grain growth and subsequently little boundary migration occurred. However, boundary migration restarted after figure 6c was taken and scars were seen to remain in the positions where the boundaries had halted. One scar appears on figure 6d and is indicated by the arrow. The scars gradually disappeared on further heating in nitrogen.

(f) *High-temperature microscopy*

In the previous experiments the specimens were all examined after cooling. In order to determine whether the boundary grooves and striations appeared whilst the silver was at the high temperature or whether they appeared during the processes of heating or cooling, specimens were examined continuously while they were maintained at high temperatures. The furnace constructed for this purpose is described in the appendix.

Figure 8, plate 12 shows a series of photomicrographs taken while a specimen was heated up to 920° C and maintained at that temperature. Figure 8a shows that after only 6 min., by which time the temperature had reached 575° C, the boundaries had appeared. Striations may be seen in figure 8c which shows the surface after 19 min. when the temperature had reached 850° C. The photomicrographs clearly demonstrate that both grain boundaries and striations are present at the high temperature and are not formed by the cooling process.

The technique provides a convenient means of observing grain growth continuously. Grain growth is seen to occur by the migration of the boundaries; the grooves move with the boundaries, leaving in general no scars at previous positions. Occasionally a network of scars is left and it is believed that the network coincides with a position of the boundaries where for some reason grain growth was temporarily halted.

When silver of commercial purity is heated in air, grain growth is retarded at the surface owing to oxidation of impurities at the grain boundaries, but Chaston (1945) has shown that in high-purity silver, grain growth proceeds at the same rate at the surface as in the centre of the material. Figure 8 should therefore be typical of what happens at the centre.

(g) *The direction of the striations*

As the striations appeared to be due to the development of specific crystallographic planes at the specimen surface, the following experiment was carried out to provide information concerning the crystallographic indices of those planes. A specimen was first heated in nitrogen at 920° C until grain growth was proceeding only slowly, and then heated in air at 920° C for $\frac{1}{2}$ hr. to produce striations. A selected field on the specimen was then photographed and the specimen heated

in nitrogen at 920° C until the striations had completely disappeared. The specimen was then compressed in a vice to produce a little plastic deformation and to show slip lines. The same field of the specimen was then photographed once more. Results are shown in figure 7, plate 11 ($\times 250$). Figure 7*a* shows the thermal etching striations. Figure 7*b* shows the slip lines. In some of the crystals there were more than one set of slip lines, but in all cases there was one set parallel to the striations previously produced by thermal etching: as slip occurs on the $\{111\}$ planes in silver and the slip lines are thus the intersections of $\{111\}$ planes with the surface, it is a reasonable conclusion that the faces of the steps causing the striated appearance are $\{111\}$ planes, since their intersection with the surface is in all cases parallel to a set of slip lines. This disagrees with the results of Graf (1942) who identified the planes as $\{100\}$ planes, but it is possible that there may be cases where the orientation of the surface of the specimen relative to crystal is such as to favour the development of $\{100\}$ planes.

(h) Summary of results

Briefly summarized, the results of the experiments may be stated as:

(i) Grain boundaries appear as grooves when silver is heated in air, oxygen, nitrogen, hydrogen and in a vacuum. They were observable in specimens heated in air at temperatures as low as 300° C.

(ii) Striations appear when oxygen is present in the atmosphere and may be caused to disappear by heating in nitrogen. The lowest temperature at which they were observed on heating in air was about 500° C. The directions of the striations were consistent with their being due to the development of $\{111\}$ faces.

(iii) Both striations and grain-boundary grooves are formed at the high temperature and are not produced by the cooling process.

(iv) When grain growth occurs the grooves move forward with the boundaries and there are not, in general, scars left at previous positions.

4. DISCUSSION

The rate of evaporation of silver in an inert gas at atmospheric pressure is but a few hundredths of that in a vacuum (Rosenhain & Ewen 1912). This is because most of the evaporating atoms are reflected after collision with the gas molecules and recondense on the surface. In effect, under these conditions silver exists in equilibrium with its vapour and an explanation of thermal etching will be sought in a consideration of the equilibrium configuration of the surface, i.e. that which has the lowest Gibbs Free Energy. Under such conditions where the nett loss of silver is negligible, any change from a polished to an etched surface occurs by the transfer of silver atoms from one part of the surface to another and the final equilibrium form will be independent of the mechanism of this transfer. In a vacuum, however, evaporation occurs without subsequent condensation and it may well be that the surface produced by this process bears no relation to the equilibrium surface.

(a) *The formation of boundary grooves*

A detailed picture of the grain boundary is not necessary for the interpretation of the grain-boundary grooves. The grain boundary must be a region of comparative atomic disorder; because of this the free energy of a polycrystalline metal is greater than that of a single crystal with the same dimensions. Formally this excess free energy may be regarded as a free energy per unit area of the crystal boundaries; this is analogous to the free energy per unit area attributed to the heterogeneous regions between different phases, in the thermodynamic description of multi-phase systems (see, for example, Guggenheim 1933).

When a metal is heated and no chemical action takes place, the only changes which can occur are rearrangements of the atoms to reduce the total free energy of the metal to a minimum. Assuming that the grains are strain free this free energy for a given specimen can be divided into three parts: (i) The free energy which the mass of the metal would possess if it were at the centre of a strain-free lattice. This is obviously constant. (ii) An additional free energy associated with the surface of the specimen. The value of the free energy per unit area associated with each element of surface may be expected to depend upon the crystallographic indices of that element of area. (iii) An additional free energy associated with the grain boundaries. The value of the free energy per unit area associated with each element of area of boundary may be expected to depend upon which crystallographic planes are in contact at this element of area, i.e. upon the relative orientation of the two crystal grains meeting at the boundary and the direction of the boundary. It is seen therefore that the approach to a minimum of free energy in a strain-free specimen must take place by the reduction of the surface and grain-boundary free energies.

Adam (1941) shows that in obtaining equilibrium conditions it is mathematically equivalent to regard a surface having a free energy per unit area as having a tensile force per unit length of the same numerical value and acting parallel to the surface. Equilibrium conditions for the grain boundaries can therefore be obtained by regarding them as the seat of surface-tension forces. At the intersection of a grain boundary with the surface, therefore, there are three tension forces acting at a line; the grain-boundary surface tension, and the surface tensions of the two crystalline faces meeting the boundary. The conditions for equilibrium therefore are given by figure 1. The plane of the figure is perpendicular to the line of intersection of the forces. T_A is the surface tension of the surface of grain A, T_B that of B, and T_{AB} the surface tension of the grain boundary. The condition for equilibrium is then $T_{AB}/\sin \gamma = T_A/\sin \beta = T_B/\sin \alpha$, and it is clear that a groove should form on the surface at the intersection of the boundary with it.

While the conditions so far considered specify the angles in the boundary grooves, their depths are controlled by the grain size, the equilibrium state being reached when each grain surface is a convex cap intersecting its neighbours at the equilibrium angles. The grooves which are observed in polished specimens represent an intermediate state in the approach to equilibrium.

No measurements have yet been made of the angle γ at the bottom of grooves, but the photomicrographs indicated that it may be small enough to mean that the free energy of the boundary is comparable with those of the crystal surfaces. While this in itself is surprising, it is possible that the free energies of the crystal surfaces have been reduced from those of clean surfaces by the presence of adsorbed gas. It is therefore suggested that quantitative measurements would have little significance except where made on perfectly clean surfaces. It is possible that grooves might not appear on such surfaces.

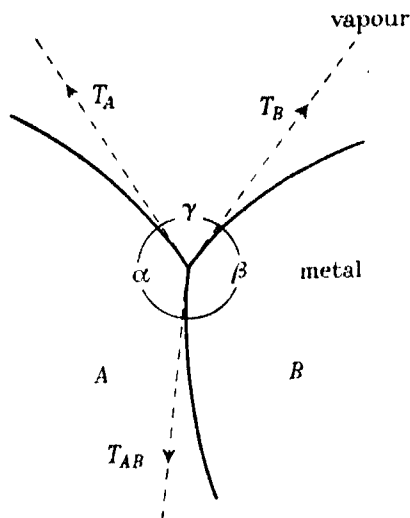


FIGURE 1

The consideration of the boundary as a seat of surface-tension forces should be significant in cases where grain growth (as distinct from recrystallization) occurs. The changes produced by the grain growth must reduce the free energy of the system, and the only manner in which this can be brought about is by reduction of the grain-boundary energy. The conditions for equilibrium at the intersection of the three grain boundaries are similar to those for the intersection of the boundary with the surface, i.e. the angles between the boundaries are governed by the relationship $T_{AB}/\sin \gamma = T_{BC}/\sin \alpha = T_{CA}/\sin \beta$, where T_{AB} is the surface tension of the boundary between grains A and B and γ is the angle made by grain C, etc. If the free energy per unit area of each boundary were a constant for that boundary and independent of its direction, the boundary area should for equilibrium be a minimum and the boundaries should be surfaces of zero curvature. A metastable state would then exist when the boundaries met at the correct angles and were surfaces of zero curvature.

Migration of the boundaries should occur in an endeavour to satisfy these conditions. However, this cannot be checked from the grain growth observed in these experiments as the surface of the specimen intersects the boundary network at an

arbitrary angle. Suitable information could be obtained by using specimens in which the recrystallized grain size was larger than the thickness of the sheet, so that the boundaries were perpendicular to the surface.

(b) *Possible mechanisms for the formation of boundary grooves*

When the silver is heated in the presence of an inert gas or in a vacuum the boundary grooves appear on the surface. Possible mechanisms for the transfer of silver from one portion of the surface to another are: slip, evaporation and condensation of silver in atomic form, surface mobility of silver atoms or ions. We shall try to estimate the relative importance of these possible mechanisms.

Slip is the normal process by which metallic crystals are plastically deformed, and effectively it is the slipping of whole atomic planes over each other in particular crystallographic directions. In view of the large forces necessary it is extremely doubtful whether the surface-tension forces are sufficient to cause any appreciable slip deformation even at high temperatures.

As suggested by Rosenhain & Ewen (1912), boundary grooves could be produced by the preferential evaporation of grain boundary metal, and the fact that they and also Fonda (1923) found that small grained metals showed a greater rate of evaporation in vacuum seems, at first sight, strong evidence for this. However, a rough calculation shows that this explanation is not adequate. To estimate the excess rate of evaporation of boundary material it will be supposed that the crystals are separated by a layer of super-cooled liquid. At a temperature T° K near the melting point T_M° K, integration of the Clausius-Clapeyron equation gives for the ratio of the vapour pressure of the super-cooled liquid to that of the solid

$$P_L/P_S = \exp \frac{F}{R} \left(\frac{1}{T} - \frac{1}{T_M} \right),$$

where F is the heat of fusion.

If the condensation coefficients of liquid and solid are the same, the rates of evaporation will be almost in the same ratio. Even at temperatures appreciably below the melting point this ratio is not much greater than unity; for silver at 900° C, for example, the ratio is 1.06. Crude as this calculation is it shows that the excess vapour pressure of the boundary material is not sufficient to explain the greater rate of evaporation when a small-grained metal is heated in a vacuum. Rosenhain & Ewen found that for a small-grained metal the loss of weight was 50% greater than for a large-grained metal. For a grain diameter of 10^{-2} cm. and a boundary of thickness 10^{-7} cm. the boundary would occupy but one fifty-thousandth of the surface area, necessitating a vapour-pressure ratio of about 2×10^4 to explain the results on these lines. The figure 10^{-7} cm. for the boundary thickness, while adequate for Kê's interpretation (1947) of the anelastic properties of aluminium, is probably too small, but it would need to be considerably increased before the increased evaporation of small-grained material could be explained.

Rosenhain & Ewen did not believe that the excess vapour pressure of the amorphous layer accounted for all the enhanced loss of weight, but thought that

some was due to evaporation from the walls of the grooves once they had formed. However, this cannot be; if we assume that the condensation coefficient of metallic atoms is unity, some of the atoms evaporating from one part of the groove condense on the opposite side. Direct application of Knudsen's Cosine Law shows that the nett evaporation from a groove is only equal to that which would occur from the plane surface occupying the neck of the groove. Nor does this small difference in the vapour pressures seem to be sufficient to explain the rapid formation of grooves which reach a depth of about 10^{-3} cm. in a few hours.

While it is maintained that Rosenhain & Ewen's and Fonda's observations of the enhanced loss of weight in small-grained material cannot be explained by the evaporation of an amorphous grain-boundary cement, the experimental fact cannot be gainsaid and further work to explain it is contemplated.

Surface mobility is probably a more important mechanism in the formation of the boundary grooves. Frenkel (1945) has shown that a necessary preliminary to evaporation is the presence of mobile atoms on the surface. Because the activation energy necessary for an atom to become mobile is less for surface migration than for evaporation followed by condensation, it is to be expected that the surface migration of atoms or ions will be a more important mechanism for the achievement of equilibrium than evaporation. Frenkel (1945) has developed a detailed theory for the change of shape caused by surface-tension forces which involves superimposing drift velocities in particular directions upon the random motion of atoms.

Andrade & Martindale (1935) have shown that surface migration occurs in silver on heating to temperatures as low as 280° C. They sputtered silver films 30 to 100 atoms thick on glass and on heating them in a vacuum of 10^{-2} mm. found that the film thickened in some places and flat crystals with $\{111\}$ faces developed leaving the silver film thinner but still continuous on the remainder of the surface. In view of Johnson's discovery (1938) that the surface structure of tungsten filaments depends upon whether they are heated by A.C. or D.C. and Mrowca's (1943) similar observations on tantalum, it is probable that while surface migration is the most important mechanism for the formation of the boundary grooves it is the migration of positive ions not neutral atoms as considered by Frenkel (1945).

The mechanism of surface migration accounts for the fact that when the grain growth occurs the boundary grooves always coincide with the instantaneous positions of the boundaries and scars seldom remain in the old positions. After the grain boundary has moved away from a particular point of intersection with the surface the free energy condition for the existence of the groove no longer holds and the equilibrium condition for that particular portion of the surface is that it should be smooth or striated. The ions then migrate over the surface and fill in the groove. If an artificial groove is made by scratching the surface, the same effect occurs; when the metal is heated, the fine structure of the scratch disappears in about 20 min. at 850° C. The occasional appearance of scars corresponding to previous positions of the grain boundaries when grain growth occurs is explained by the fact that if for any reason the boundary halts for some time in one position

the groove will get deeper with time and when the boundary moves away from that position the grooves take longer to fill in. If the grooves were due to preferential evaporation of grain-boundary material, then during grain growth material would be lost more or less evenly over the surface of the growing grain and there would be a step rather than a groove at the grain boundary.

The complete reversibility of the processes by which the striations appear and disappear when the silver is alternately heated in oxygen and nitrogen suggests that the striations exist in equilibrium with an atmosphere containing oxygen and are not merely the result of a particular mechanism of evaporation or oxidation. It is supposed that the presence of the oxygen modifies the equilibrium configuration of the silver surface, so that a stepped structure in which specific crystallographic planes are developed has less energy than a smooth surface of less area but at arbitrary orientation. If this is so, the free energy per unit area of the specific planes developed must be significantly smaller in an environment of oxygen than that of other planes.

That, for an ionic crystal, the free energy per unit area of a crystal face depends on its crystallographic direction was shown by Lennard-Jones & Taylor (1925), who found by calculation that for rock salt the surface energy of a {110} face is almost four times the surface energy of a {100} face, so that in equilibrium the {100} face would be expected to develop preferentially. Lukirsky (1945) found that on heating a spherical crystal of rock salt it developed crystallographic facets and changed its shape to that of a polyhedron.

Since in inert atmospheres no striations appear, it may be assumed that any difference in the free energies per unit area of different crystallographic planes is too small to cause the formation of striations with the consequent increase of area. In oxygen, however, the relative values of free energies per unit area must be considerably modified. The possible interactions between the silver and the oxygen are: solution of oxygen in silver, the formation of an adsorbed monolayer on the surface of the silver, and the existence of silver oxide molecules in the vapour phase. Because the amount of oxygen dissolved in silver is small, increasing only to about 2 atomic per cent at the melting point (Steacie & Johnson, 1926), and because the partial pressure of silver oxide in the vapour phase will be small, it is probable that the most important effect is the preferential adsorption of oxygen on different faces. Direct experiments on the heterogeneous equilibrium of silver and oxygen are not sufficiently sensitive to show the presence of molecular oxide in the vapour phase; it must therefore be small compared with the equilibrium pressure of oxygen, but it is probably a number of times greater than the partial pressure of atomic silver vapour. Its existence may, however, be inferred from the enhanced evaporation of silver in the presence of oxygen, it being supposed that silver evaporates in the form of molecular oxide.

When silver is heated in air or oxygen at atmospheric pressure it will evaporate in the forms of atomic silver and molecular oxide. As for evaporation in the presence of an inert atmosphere it will be assumed that most of the evaporating atoms and

molecules are reflected and recondense on the surface so that the silver exists in equilibrium with its surroundings. Under these conditions, by the principle of detailed balancing, each process of evaporation will be balanced by the condensation of an equal amount of the same constituent.

In a consideration of the mechanisms whereby the striated equilibrium-surface configuration may be approached in an atmosphere of oxygen all three mechanisms—slip, atomic evaporation and condensation, and surface migration, which may contribute to the formation of boundary grooves, and in addition the evaporation and condensation of molecular silver oxide—must be considered. In so far as the evaporation of molecular silver oxide tends to expose certain crystallographic planes it may be interpreted as the preferential attack of those planes by the oxygen, but this is not the only mechanism as was suggested by Leroux & Raub. There must be redistribution of the silver by surface migration, evaporation and subsequent condensation of silver atoms and the condensation of oxide from the vapour phase. It is impossible to estimate the relative importance of the contributions of these mechanisms to the attainment of the final surface configuration, but that the transfer of material without the formation of the oxide is an important mechanism is clearly demonstrated by the fact that the striations disappear without appreciable loss of weight when the specimen is heated in nitrogen.

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APPENDIX

A furnace for high-temperature microscopy

The requirements set in the design of a furnace for use in the microscopic examination of specimens at high temperatures were that it could be used with a microscope objective having a useful magnification up to 250; that fairly large areas of the specimen could be scanned by movement of the specimen relative to the objective; and that the specimens could be examined in various atmospheres and at temperatures up to the melting point of silver. Furnaces for high-temperature photomicrography have been described by Esser & Cornelius (1933) and by Swinden Howie & Chesters (1939), but neither meets all these requirements.

The limiting feature in the design of such a furnace is the working distance of the objective. For objectives with the necessary numerical aperture for the magnifications required, the distance between the hot specimen and the objective, which has to remain cool, is small and this necessitates very efficient insulation of the specimen and cooling of the objective. For the highest magnifications it was decided to use a 16 mm. achromatic objective with 0.28 numerical aperture and

a working distance of 7 mm.; this has a maximum useful magnification of about 250. In view of the short working distance it was decided to use gas or a vacuum for thermal insulation rather than a porous refractory, and reduce radiation losses by silver plating all hot surfaces. The furnace finally constructed is shown in figure 9. The base of the furnace, made of mild steel, stands on three adjustable legs on the

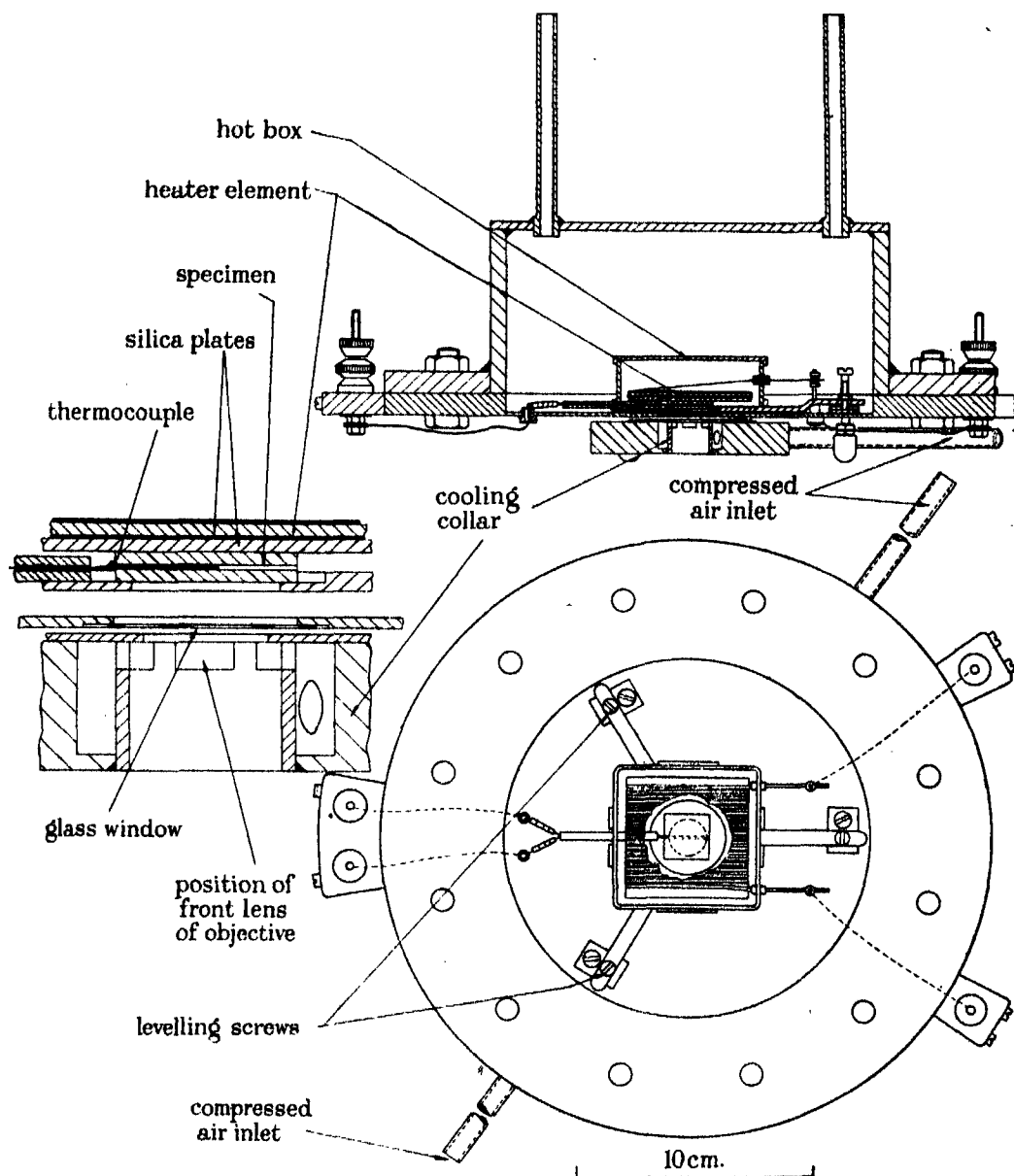


FIGURE 9. Furnace for high-temperature microscopy.

specimen support of a Vickers projection microscope. At the centre of the base is a glass window consisting of a microscope cover glass which is sealed in position by means of I.C.I. high-temperature optical cement. The specimen—a 2 cm. square piece of 8 s.w.g. silver—is supported above and about 4 mm. away from the window, on a stand made of heat-resisting steel. The specimen rests over a circular hole in the centre of the stand. The stand, which consists of a square plate with three radiating arms, is supported by adjustable screws at the ends of the arms; the screws have spherical ends and rest in grooves in the base of the furnace. Above the specimen is placed a sheet of silica $\frac{1}{16}$ in. thick and on this rests the heater which consists of nichrome tape (0.1×0.002 in.) wound on a similar silica sheet. Heater and specimen are enclosed in a box made of heat-resisting steel. The whole is enclosed by a cylindrical cap of mild steel which is provided with a flange and may be bolted to the base to form, with a synthetic rubber gasket, a gas-tight enclosure. Inlet and outlet tubes are supplied in the cap for the atmosphere required for the test. The specimen is drilled so that a thermocouple may be inserted at its centre, and the thermocouple leads pass out through the wall of the heat-resisting steel hot-box by means of alumina insulators, as do the heater wires. Both thermocouple leads and heater leads pass out of the furnace through silvered porcelain insulators which are soldered into the base. The thermocouples are waxed into the insulators and the heater current is carried in copper wires which are soldered to the insulators. All the portions of the hot-box are silvered to reduce radiation losses and the supporting arms and screws are thin to reduce conduction. The upper surface of the mild steel base is silver plated and polished to reflect radiant heat.

Below the mild-steel base is the cooling collar which rests on the microscope specimen support. The legs of the furnace base are adjusted so that there is a distance of about 1 mm. between the collar and the base. The microscope objective lies in the central space of the cooling collar with its front lens a little below the level of its top surface. Compressed air is supplied at an initial pressure of 10 lb./sq.in. through the two inlet tubes and allowed to expand into the annular space inside the collar. After expanding in this space it flows on to the surface of the lens and thence radially outwards between the collar and the furnace base, thus cooling both objective and glass window. Experiments using a dummy objective carrying a thermocouple showed that the temperature of the front lens did not rise more than two or three degrees above room temperature.

It has been found that a specimen temperature of 920°C can be maintained with a power consumption of 300 W. Because of the small heat capacity of the furnace it is not possible to regulate the temperature with a commercial controller. The current is therefore supplied from a constant-voltage transformer and this enables the temperature to be controlled by hand to within 2°C without too frequent attention. When setting up the furnace, the height of the base is first adjusted to give the required clearance between it and the collar, then with the objective front lens just below the top surface of the collar the specimen is levelled and its height adjusted by means of the screw supports of the hot-box. The specimen is set a little

below the correct height for focus in order to allow for expansion when the apparatus heats up. Afterwards, when the cap is on and the furnace running, focusing is achieved by means of the microscope fine adjustment which moves the objective.

Difficulty was experienced with a form of contamination which has not yet been fully explained. It was found that after a period of heating in the furnace striations gradually disappeared, the process spreading slowly over the surface. It was found by auxiliary tests that this could be caused by contamination of the surface by some component of the heat-resisting steel. Although this has been reduced by the silver plating on the steel, investigations still have to be limited to 3 hr. The thermocouple and heater wires also form possible sources of contamination. This effect is being investigated in detail.

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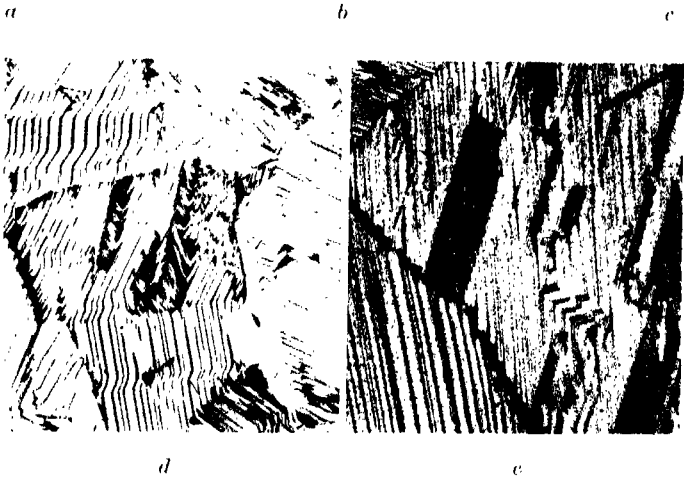


FIGURE 2

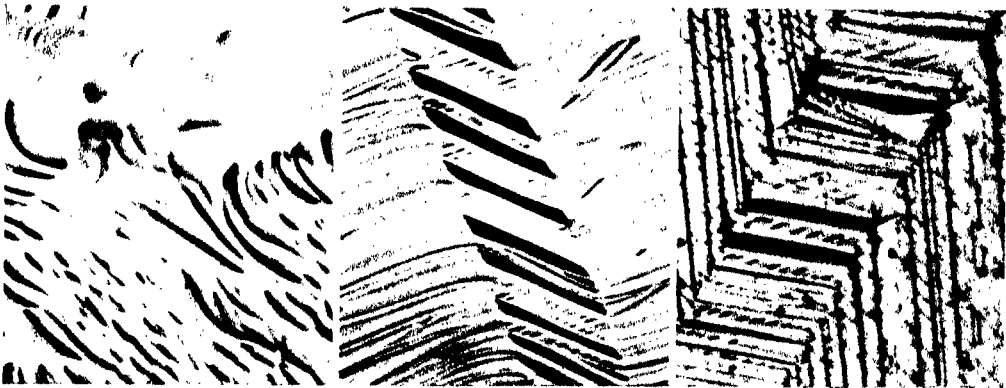


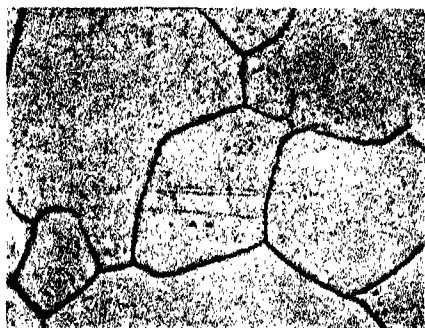
FIGURE 3



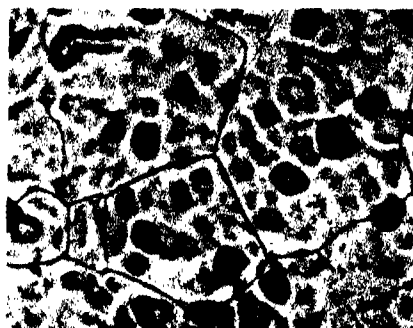
a



b

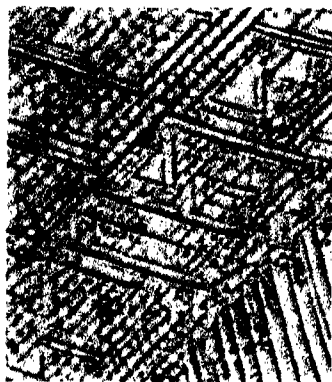


c



d

FIGURE 4



a



b



c

FIGURE 5

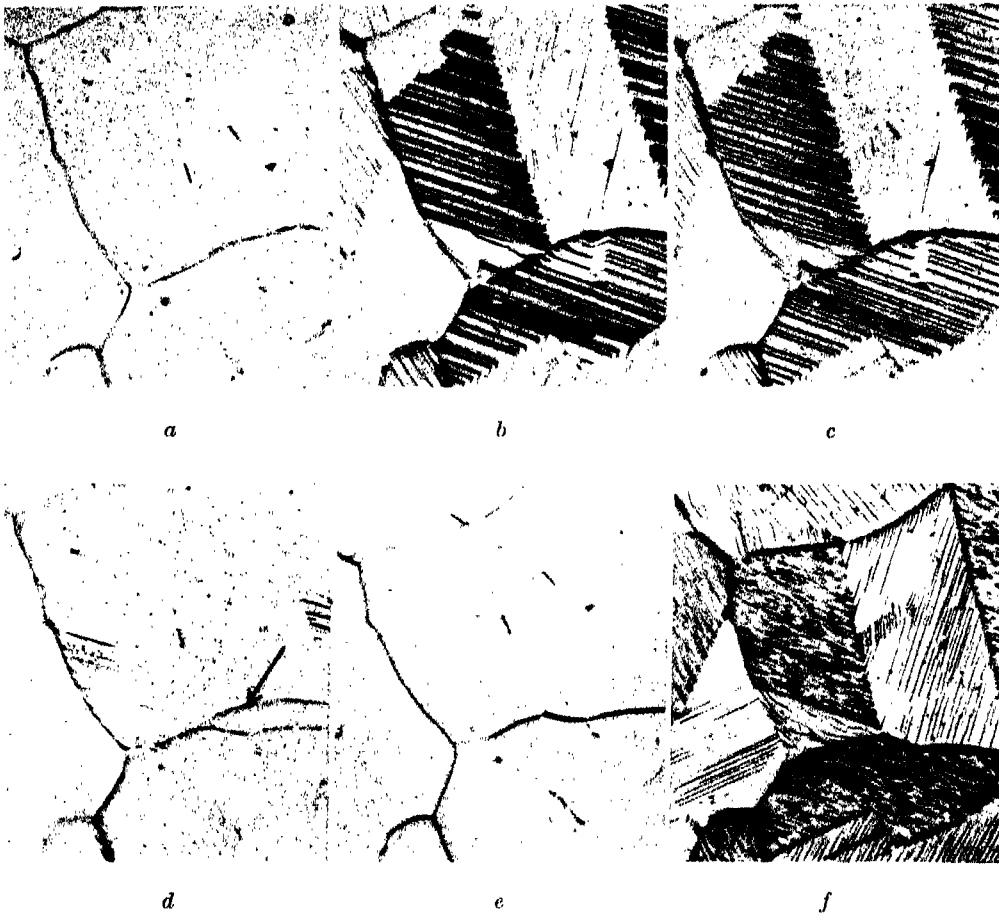


FIGURE 6

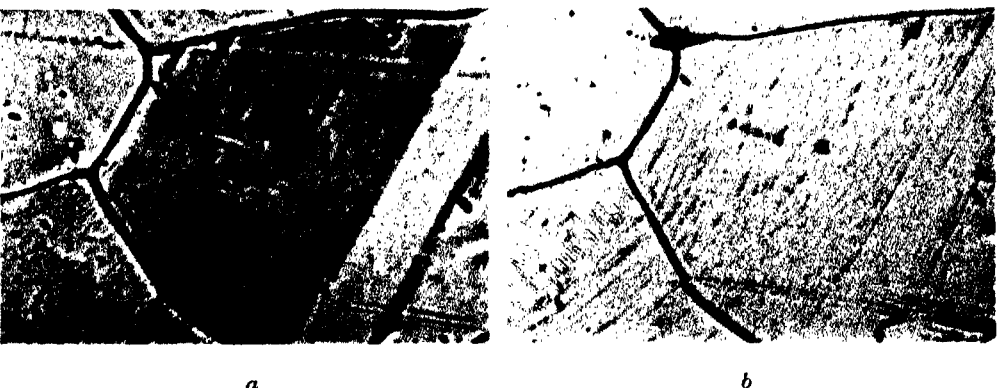


FIGURE 7

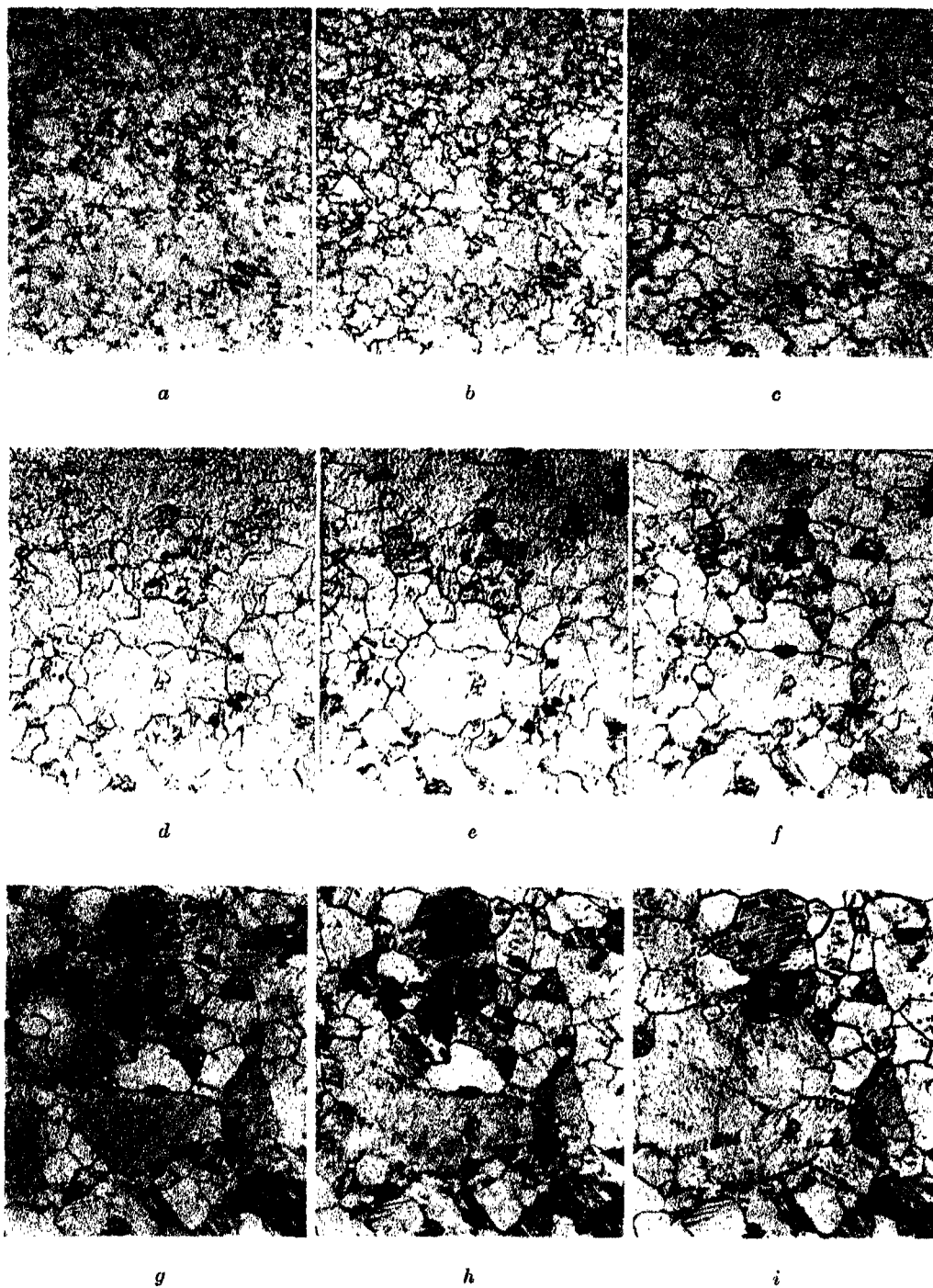


FIGURE 8

DESCRIPTION OF PLATES 9 TO 12

PLATE 9

FIGURE 2. Silver heated in air for 11 hr. at different temperatures. (a) 300° C. (b) 500° C. (c) 700° C. (d) 850° C. (e) 940° C. ($\times 250$.)

FIGURE 3. Silver heated in air for 11 hr. at different temperatures. (a) 500° C. (b) 850° C. (c) 940° C. ($\times 1500$.)

PLATE 10

FIGURE 4. Silver heated in different atmospheres at 920° C. (a) 11 hr. in air. (b) 11 hr. in oxygen. (c) 11 hr. in nitrogen. (d) 1½ hr. in a vacuum. ($\times 250$.)

FIGURE 5. Some etch patterns obtained on silver heated in oxygen for 11 hr. at 920° C. ($\times 2000$.)

PLATE 11

FIGURE 6. The reversibility of striations. Silver heated at 920° C. (a) 11 hr. in nitrogen. (b) Same field after 1 hr. in air. (c) After a further 1 hr. in nitrogen. (d) After a further 2 hr. in nitrogen. (e) After a further 8 hr. in nitrogen. (f) After a further 1 hr. in air. ($\times 250$.)

FIGURE 7. The determination of the planes causing the striations. (a) Silver showing striations produced by heating in air. (b) Silver showing slip lines due to deformation after the etching striations had been removed by heating in nitrogen. ($\times 250$.)

PLATE 12

FIGURE 8. High-temperature microscopy. Photomicrographs of a silver specimen taken while the specimen temperature was raised at 920° C and maintained at that temperature in air. Same field throughout. ($\times 100$.) (b) After 6 min. temperature up to 575° C. (b) After 9 min. temperature up to 670° C. (c) After 19 min. temperature up to 850° C. (d) After 25 min. temperature up to 900° C. (e) After 40 min. temperature up to 917° C. (f) After 50 min. temperature up to 927° C. (g) After 60 min. temperature at 920° C. (h) After 70 min. temperature at 920° C. (i) After 90 min. temperature at 920° C.

The theory of the galvanomagnetic and thermomagnetic effects in metals

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The methods of a previous paper are used to discuss the effect of a magnetic field on the thermoelectric power of a metal containing two overlapping energy bands of normal form. Exact solutions of the transport equation are obtained for the three limiting cases of high temperatures, low temperatures and very strong magnetic fields, and it is shown that the formulae can be generalized to give approximate expressions for all temperatures and all fields. The magnetic change of the thermoelectric power is found to be small at very low and high temperatures, and to pass through a maximum at intermediate temperatures.

The transverse galvano- and thermomagnetic effects are also considered, and the formulae which hold for free electrons are generalized so as to be approximately valid for all temperatures. For free electrons, the Hall coefficient remains constant as the temperature decreases, the Righi-Leduc coefficient increases, and the Ettingshausen and Ettingshausen-Nernst coefficients decrease and change sign at very low temperatures. The corresponding formulae for a metal containing two bands are also obtained, and are used to show that the theoretical predictions for free electrons cannot hold for real metals except in special cases. Finally, the two-band model is used to discuss the effect of the magnitude of the magnetic field on the coefficients of the transverse effects.

1. INTRODUCTION

1.1. The present paper is a sequel to a previous one (Sondheimer & Wilson 1947; subsequently referred to as I*), and continues the investigation by the methods of the modern theory of metals of the various effects which occur when a metallic conductor carrying an electrical or thermal current is placed in a magnetic field. The so-called galvanomagnetic effects arise when the primary current is electrical, and the thermomagnetic effects when it is thermal. The effects can also be subdivided into 'transverse effects in a transverse magnetic field', where the primary current and the electric field or temperature gradient of interest are at right angles to each other and to the magnetic field, 'longitudinal effects in a transverse magnetic field' where they are parallel to each other but at right angles to the magnetic field, and 'longitudinal effects in a longitudinal magnetic field' where they are parallel to each other and to the magnetic field. The second and third groups of phenomena include the magneto-resistance effects which have been discussed in I and the influence of a magnetic field on the thermoelectric power which will be considered in the present paper. The most important examples in the first group, also to be discussed below, are the four effects which are often referred to simply as the 'transverse galvano- and thermomagnetic effects'. These effects are usually described

* There is an error in equation (70) of paper I. The index of the last factor on the right-hand side should be -2 instead of -1 .

by certain coefficients which may be defined by considering a metal strip with its surface in the xy -plane, carrying an electric current J_x or a thermal current w_x in the x -direction and subjected to a magnetic field H in the z -direction. The following cases are then of practical importance:

If $J_x \neq 0$ but the transverse current $J_y = 0$, there exists a transverse electric field $\mathcal{E}_y$. The ratio $\mathcal{E}_y/HJ_x$ is known as the Hall coefficient A_H .

If $J_x \neq 0$ and $w_y = 0$, there exists a transverse temperature gradient $\partial T/\partial y$, and the ratio $(-\partial T/\partial y)/HJ_x$ is known as the Ettingshausen coefficient A_E .

If $\partial T/\partial x \neq 0$ and $J_y = 0$, then $\mathcal{E}_y \neq 0$ and the ratio $\mathcal{E}_y/(-H\partial T/\partial x)$ is known as the Ettingshausen-Nernst coefficient B_{EN} . The experimental values are also sometimes expressed in terms of the ratio $\mathcal{E}_y/Hw_x$, which is denoted by A_{EN} . Clearly $A_{EN} = B_{EN}/\kappa$, where κ is the thermal conductivity.

If $\partial T/\partial x \neq 0$ and $w_y = 0$, then $\partial T/\partial y \neq 0$ and the ratio $(\partial T/\partial y)/(H\partial T/\partial x)$ is known as the Righi-Leduc coefficient B_{RL} . An alternative coefficient is defined by

$$A_{RL} = (-\partial T/\partial y)/Hw_x = B_{RL}/\kappa.$$

In many cases the thermal conditions in the y -direction are not specified, and it is then necessary to distinguish between 'adiabatic' conditions where $w_y = 0$ and 'isothermal' conditions where $\partial T/\partial y = 0$. The consequences of this distinction are discussed in more detail in § 2.

The calculations can be completed and the results compared with experiment only if the metal is represented by a sufficiently simple model. In the simplest possible case the electrons are assumed to be quasi-free, the energy being proportional to the square of the wave-vector. The results for this model have so far only been worked out for the case of high temperatures (Sommerfeld & Frank 1931; Kohler 1941 *a*), where it gives the correct order of magnitude (disregarding the sign) of the four transverse effects in the limit of vanishingly small magnetic field. In the present paper the theory is extended to cover the case of arbitrary temperature. The free electron model, however, fails entirely to account for the magneto-resistance effects, which are zero for a model in which the surfaces of constant energy form a single family of spheres (Peierls 1931). It has proved impossible so far to carry out the calculations even part of the way with a model which shows all the peculiarities that the energy surfaces are likely to have in real metals. It is therefore necessary to discuss a model which is more general than the free electron model and which gives a non-zero result for the magneto-resistance effects, but which is sufficiently tractable for the calculations to be completed. The only model so far proposed which fulfils these requirements postulates the existence of two overlapping energy bands, an s -band containing some conduction electrons and a d -band containing some unoccupied levels; in each band the energy is assumed to be proportional to the square of the wave-vector. In I it has been shown that this model gives a satisfactory account of the magneto-resistance effects which occur in a transverse field, over the whole range of temperatures and magnetic fields. In the present paper the same model is used to discuss the effect of a magnetic field on the thermoelectric power,

particularly at low temperatures where the effect is most pronounced but where the theory is more difficult owing to the non-existence of a time of relaxation. It is not necessary to consider the remaining thermoelectric effects, since they can all be expressed in terms of the thermoelectric power (see, for example, Wilson 1936, §§ 5.41 to 5.43). Also, as in I, the case of a longitudinal magnetic field has to be excluded, since the two-band model is not sufficiently general to give a non-zero result for this case.

The two-band model is further used to obtain formulae for the transverse effects in the limit of zero magnetic field. At best, the free electron model can only be expected to apply to the alkali metals, and it is therefore again necessary to investigate more complicated models, so as to determine whether the theoretical results obtained for free electrons can be expected to apply to metals in general, and, if they do not apply, to suggest at least qualitatively how they can be generalized. Finally, the two-band model is used to derive formulae for the field dependence of the transverse effects. As in the case of the electrical and thermal conductivities, the influence of a magnetic field on the coefficients of the transverse effects is determined by the departure of the energy surfaces from spherical symmetry, and the two-band model is therefore the simplest which can be expected to give even qualitatively correct results.

1.2. The metals to which the two-band model can be directly applied and in which the *s*- and *d*-bands have immediately obvious physical meanings consist of the transition elements (excluding the ferromagnetic metals when transport effects are being considered). It was, however, pointed out in I, p. 448 that the model could be applied to other metals provided that the parameters were suitably defined. An expanded form of the argument in which the assumptions are more explicitly stated is as follows.

The energy surfaces in *k*-space (*k* being the electron wave-vector) have a very complicated structure even for the simplest of metals such as the alkalis (see, for example, Sommerfeld & Bethe 1933, p. 400, figure 23). It is, however, possible to give a formal theory of all the transport phenomena provided that the assumption is made that a time of relaxation exists (e.g. Wilson 1936, chapter v). The various physical quantities can then be expressed in terms of the time of relaxation τ , the energy *E*, the derivatives of *E* with respect to *k*, and in some cases the derivatives of τ with respect to *k*. Unfortunately, a time of relaxation does not exist for a general model, and the only cases in which the formal theory applies is when *E* is a function of $|\mathbf{k}|$ only, and even then only at high temperatures. To make any further progress it is necessary to make simplifying assumptions, which are usually indicated by the structure of the expressions which occur in the formal theory. If one wishes to carry out the calculations completely (and this is essential if one wishes to discuss low temperature phenomena at all), it is necessary to choose the simplest possible model which contains the features which are shown to be essential in the formal theory. For example, in the formal theory the electrical conductivity only depends

upon τ and the first derivatives of E ; and in fact only the squares of the latter occur. It is therefore unnecessary, if one restricts oneself to order of magnitude calculations, to consider a model in which the first derivatives change sign. This is the justification for the very wide use of the free electron model for discussing the electrical conductivity of metals whether monovalent or not. In some ways it is better to use the two-band model for divalent metals since the meaning of the parameters becomes clearer, and it is possible to see whether, for example, the average effective mass of the electrons is the arithmetic or harmonic mean of the effective masses of the individual electrons. If, however, the parameters in the more general models cannot be distinguished by experiment from those for simpler models, it is best to choose the simplest model that gives a non-zero result.

In general, the magnetic effects involve the second derivatives of the energy linearly, and the simple free electron model is inadequate even for the alkalis. The real energy surfaces have a complicated structure and consist of portions having positive curvature and portions having negative curvature (but it must be remembered that only those energy levels near the highest occupied level play a part). The two-band model is the simplest model having this property, the s -band having positive and the d -band having negative curvature. It does not, however, have all the properties required. For example, in a real metal the relevant portions of the energy surface which have negative curvature may not form a continuous domain, nor will they necessarily possess a maximum energy level. But such factors as these do not affect the calculations at all, though they have a strong bearing on the physical interpretation of the parameters. In a transition element the d -band has an obvious physical significance, and the number of vacancies in it can be defined as the number of electrons required to fill the uncompleted inner shell, so that the two-band model is easy to interpret. In the case of a monovalent or divalent metal there is no inner shell to complete, but one can still consider the d -band of the two-band model to be a reasonable representation of those portions of the energy surfaces that have negative curvature.* However, it is not possible to determine the number of vacancies to be ascribed to the d -band in the same kind of way as for the transition elements, and in the present state of the theory one can only treat it as a parameter of the same order of magnitude as the number of atoms. If one had to assume that it was of a very different order of magnitude, the physical interpretation would obviously be at fault.

It is possible to introduce further refinements into the two-band model to make it correspond more closely to reality. For example, one could introduce s - d transitions, corresponding to transitions in which the initial and final states lie in the regions of positive and negative curvature respectively. Such refinements, however, seem

* In a divalent metal the conduction bands are better labelled lower and upper bands to avoid the implication that the symbols ' s ' and ' d ' have any physical significance. The conduction bands cannot be strictly labelled s , p , d , ... bands, but are mixed s - p bands. The first and second bands are both partially filled with electrons, and the energy levels which determine the conduction properties are primarily of negative curvature in the lower band and of positive curvature in the upper band.

unnecessary in the present state of development where the experimental data are so inadequate.

To sum up, the two-band model assumes that only derivatives of the energy up to the second are important. It is then the most general model required for isotropic metals, and the calculations can be carried out for all temperatures. The model could be generalized to deal with anisotropic metals, but the calculations would then have to be restricted at best to high temperatures where a time of relaxation exists, since it has not so far been possible to extend the theory to anisotropic metals at low temperatures. (It should be noted, however, that no proof has yet been given that a time of relaxation exists for anisotropic metals even at high temperatures.) The model breaks down (as do all models so far proposed) if derivatives of the energy of the third or higher orders are important, and in certain cases if the derivatives of τ have to be taken into account. According to this criterion the model must fail for those galvanomagnetic and thermomagnetic effects which occur in a longitudinal magnetic field, but should be sufficient to deal with the order of magnitude of the effects which occur in a transverse field. If in the future it is found that there is a substantial difference in the behaviour of transition and multivalent metals as regards the effects discussed here, the conclusion would be that a much more elaborate theory of the magnetic effects is required than the one given here. But such evidence as exists does not suggest any such fundamental difference, and it is therefore reasonable to proceed on the basis of the simplest possible assumptions. It is very desirable, however, that some model should be investigated for which $\partial\tau/\partial E$ behaves anomalously.

1.3. In § 2 the formal expressions for the various effects are obtained according to the two-band model, and in § 3 expressions are given which, together with formulae already obtained in I, represent the complete solutions in the three limiting cases of very high and very low temperatures and very strong magnetic fields.

It was shown in I that, although it is not possible to solve the transport equation in the general case, simple approximate 'interpolation formulae' can be set up for the magneto-resistance effects which reduce to the correct expressions in the three limiting cases for which the exact solutions are known. In § 4 the thermoelectric power is considered, and it is shown that it is again possible to generalize the exact solutions so that they can be used over the whole temperature range. To do this, simple interpolation formulae are set up for the thermoelectric power and the adiabatic Ettingshausen-Nernst coefficient of a metal containing a single band, corresponding to the known expressions for the electrical and thermal conductivities (Wilson 1937). These formulae make it possible to determine the generalized forms of all the quantities required for discussing the two-band model, satisfying the usual criterion of reducing to the exact expressions in the limiting cases of high temperatures, low temperatures and strong magnetic fields. It is thus possible to calculate general expressions of approximate validity for all the effects to be considered in the present paper.

The change of the thermoelectric power in a magnetic field at various temperatures has been investigated experimentally by Grüneisen & Erfling (1939) for beryllium. The effect is found to be small at high and very low temperatures and to pass through a maximum value at an intermediate temperature, the position of the maximum moving towards higher temperatures as the magnetic field is increased. It is shown in § 4.21 that the predictions of the two-band model are in general agreement with this behaviour.

The free electron model has been used by Sommerfeld & Frank (1931) and Kohler (1941*a*) to discuss the transverse effects in the special case where it is legitimate to assume that a time of relaxation exists. The results for this case, which are only valid for high and extremely low temperatures, are summarized in § 5.1. The generalized formulae which are approximately valid over the whole temperature range are given in § 5.2. These formulae show that, for free electrons, A_H is negative and independent of the temperature for all temperatures, B_{RL} is negative and increases in absolute value as the temperature decreases, while B_{EN} and A_E are positive at high temperatures, decrease as the temperature decreases, and at very low temperatures they reverse in sign, pass through a minimum value and eventually tend to zero as T approaches zero. Similar results hold for a single d -band, except that A_H and B_{RL} are positive instead of negative.

In § 5.3 the extent to which the two-band model modifies these results is investigated, and it is shown that the theoretical predictions for free electrons cannot be expected to apply to real metals except in special cases. In particular, the two-band model allows A_H to vary with the temperature, and B_{EN} and A_E need no longer become negative at very low temperatures. Further, the simple relations among the coefficients which hold for free electrons are, in general, no longer valid for the two-band model, and are therefore not generally true. However, the two-band model fails to account for the negative values of B_{EN} and A_E which are observed in some metals at high temperatures; the explanation of these anomalous signs would require a still more complicated model, with the property that the time of relaxation is a decreasing function of the wave number at the surface of the Fermi distribution.

In § 6 the two-band model is used to derive formulae for the field dependence of the transverse effects, and these are used to give a qualitative discussion of the behaviour of the coefficients in a magnetic field of arbitrary magnitude. The Hall coefficient has already been discussed by Jones (1936) in the case of high temperatures, where a time of relaxation exists. It is shown in § 6 that a formula of the same form can be used over the whole temperature range, and a similar formula is obtained for B_{RL} . The behaviour of B_{EN} and A_E is, in general, complicated and only some simple special cases are discussed; in particular, the form of the coefficients in the limit of very strong magnetic fields is considered.

1.4. The experimental data on the transverse effects with which to compare the theory are discussed in § 7. They are both inadequate and confusing. Results reported by different workers differ by factors of up to 80 (compare Borelius 1935; Meissner

1935); it is very seldom that the various effects have been measured on the same specimen and no attention seems to have been paid to choosing metals for which the theoretical interpretation would be relatively easy. The inconsistency of the results available is shown in table 1 *infra*, where data are given for a quantity which should by thermodynamic arguments be unity but which differs very considerably from it. If we disregard ferromagnetic metals, strongly anisotropic metals such as bismuth and discard results which differ by a factor of more than 2 when measured by two different experimenters, there is very little experimental evidence left. Further, there are no data at all for those metals in which the parameters for the separate *s*- and *d*-bands can be estimated from other phenomena, so that it is only possible at present to attempt to verify the theory as regards orders of magnitude, and even then only by applying the principles laid down in § 1.2 *supra* and in I, p. 448 for interpreting the parameters.

The position is even worse for the temperature variation of the transverse effects than for the orders of magnitude of the effects at room temperatures since, except for the Hall effect, there are at present no data at all for any metals at low temperatures. On the other hand, at ordinary temperatures (where some measurements exist) the results of the present theory are in all essential respects identical with those of the old treatments, and new effects are to be expected at low temperatures only (see § 5). Further, at room temperatures and for normal metals the effect of the magnitude of *H* on the coefficients is negligible, whereas at sufficiently low temperatures the fields that are obtainable in practice are adequate to observe the effects (discussed in § 6) which occur when the magnetic field is very strong. For a verification of the new predictions of the present theory as regards the temperature and field variation of the coefficients experiments at low temperatures are therefore essential, and further discussion must be postponed until such experimental evidence has become available.

2. GENERAL FORMULAE

In the two-band model, which has been described in I, there are two overlapping partially filled bands of normal form, the *s*- and *d*-bands. The general expressions obtained on the basis of this model for the electrical and thermal currents in an arbitrary transverse magnetic field have been given in I (equations (13) to (16)), and it has been shown there that these equations can be used to express all the physical quantities of interest in terms of certain coefficients $i^{(n)}$ which depend on the magnetic field and on the *s*- and *d*-electron variables. Only the expressions for the electrical and thermal conductivities σ and κ were deduced in I, and it is now necessary to calculate the corresponding expressions for the thermoelectric power and the transverse effects.

When a temperature gradient $\partial T/\partial x$ is maintained along a strip of metal but no electric current is allowed to flow, a longitudinal electric field $\mathcal{E}_x$ is set up, and if this is written in the form

$$-e\mathcal{E}_x = \frac{\partial \xi}{\partial x} + \mathcal{O}\frac{\partial T}{\partial x},$$

$-\epsilon$ being the electronic charge and ζ the Fermi energy level, then $-\mathcal{S}/\epsilon$ is known as the absolute thermoelectric power per degree. It will be assumed, as in the case of the thermal conductivity, that $\mathcal{S}$ is measured under adiabatic conditions, the thermal conditions in the y -direction being such that $w_y = 0$. Using this condition in addition to $J_x = J_y = 0$, it is found by means of I, equations (13) to (18), that

$$\mathcal{S} = k^2 T \frac{(P_s - P_d) \{(V_s + V_d)(X_s + X_d) - (W_s - W_d)(Y_s - Y_d)\} + (Q_s + Q_d) \{(V_s + V_d)(Y_s - Y_d) + (W_s - W_d)(X_s + X_d)\}}{\{(V_s + V_d)^2 + (W_s - W_d)^2\}(X_s + X_d)}, \quad (1)$$

where k is Boltzmann's constant, V, W, X, Y are certain combinations of the $i^{(n)}$'s defined by I, equations (20) and (22), while

$$\zeta^2 P = i_s^{(1)} - \zeta i_1^{(1)}, \quad \zeta^2 Q = i_s^{(3)} - \zeta i_4^{(1)}, \quad (2)$$

and the suffixes s and d refer to the s - and d -band respectively.

The coefficients of the transverse effects are calculated similarly. In the case of the Hall effect, $J_x \neq 0$, while $J_y = 0$ and the specimen is kept at uniform temperature, so that $\partial T/\partial x = \partial T/\partial y = 0$. It is then found that

$$A_H = -\frac{3\pi^2 \hbar^4}{\epsilon^2 H} \frac{W_s - W_d}{(V_s + V_d)^2 + (W_s - W_d)^2}. \quad (3)$$

For the Ettingshausen effect $J_x \neq 0$, while $J_y = \partial T/\partial x = w_y = 0$, and

$$A_E = \frac{3\pi^2 \hbar^4 T}{\epsilon H} \frac{(Q_s + Q_d)(V_s + V_d) - (P_s - P_d)(W_s - W_d)}{\{(V_s + V_d)^2 + (W_s - W_d)^2\}(X_s + X_d)}. \quad (4)$$

The experimental conditions assumed here are never strictly fulfilled in practice, since the condition $w_y = 0$ is at best only approximately valid, but the experimental values are usually corrected for any heat lost to the surroundings (compare Meissner 1935, p. 365). A further correction is necessary if there is any temperature difference between the ends of the specimen.

The Ettingshausen-Nernst effect is measured with $\partial T/\partial x \neq 0$, while $J_x = J_y = 0$ and $w_y = 0$ (adiabatic conditions). Denoting the adiabatic coefficient by B_{EN}^2 , it is found that

$$B_{EN}^2 = \frac{k^2 T}{\epsilon H} \frac{(Q_s + Q_d) \{(V_s + V_d)(X_s + X_d) - (W_s - W_d)(Y_s - Y_d)\} - (P_s - P_d) \{(V_s + V_d)(Y_s - Y_d) + (W_s - W_d)(X_s + X_d)\}}{\{(V_s + V_d)^2 + (W_s - W_d)^2\}(X_s + X_d)}. \quad (5)$$

The experimental values must, however, differ from this quantity, since they are obtained without allowing for the thermoelectric field which is always present in the leads used to measure the transverse potential difference. A general discussion of this question has been given by Kohler (1941*b*) who has shown that, if certain reasonable assumptions are made, the apparent value of the adiabatic coefficient turns out to be identical with the isothermal coefficient. This result is readily shown to follow also from the present equations, which are merely particular cases of Kohler's; the proof follows exactly the same lines as his and the details are left to

the reader. It will accordingly be assumed that the value of the Ettingshausen-Nernst coefficient which is actually measured is obtained by using the condition $\partial T/\partial y = 0$ instead of $w_y = 0$. Denoting this value by B_{EN}^t , it is found that

$$B_{EN}^t = \frac{k^2 T}{eH} \frac{(Q_s + Q_d)(V_s + V_d) - (P_s - P_d)(W_s - W_d)}{(V_s + V_d)^2 + (W_s - W_d)^2}. \quad (6)$$

Finally, for the Righi-Leduc effect $\partial T/\partial x \neq 0$, while $J_x = J_y = 0$, $w_y = 0$, and

$$B_{RL} = -\frac{1}{H} \frac{Y_s - Y_d}{X_s + X_d}. \quad (7)$$

The measured values have again to be corrected for any heat which is lost to the surroundings.

3. SPECIAL SOLUTIONS

The quantities V , W , etc. which appear in equations (1) to (7) can be evaluated explicitly in the three limiting cases of high temperature and arbitrary magnetic field, low temperature and arbitrary magnetic field, and high magnetic field and arbitrary temperature. The method of calculation has been described in I and the resulting expressions for V , W , X , Y have been given there (equations (27), (28), (42) to (48)), and it is now only necessary to supplement these results by giving the corresponding expressions for P and Q . The calculations follow the same lines as before, and only the results will be quoted here. For the details of the method and for the notation the reader is referred to I, § 3.

3.1. High temperatures.

$$P = \frac{1}{3}\pi^2 \frac{\partial V}{\partial \zeta}, \quad Q = \frac{1}{3}\pi^2 \frac{\partial W}{\partial \zeta}, \quad (8)$$

where V and W are given by I, equation (27).

3.2. Low temperatures.*

$$\zeta P = \frac{1}{3}\pi^2 (2m\zeta)^{\frac{1}{2}} \frac{\beta \zeta^{\frac{1}{2}} (2\alpha^2 + \beta^2 \zeta)}{(\alpha^2 + \beta^2 \zeta)^2} + \left(\frac{T}{\Theta}\right)^3 \left\{ \mathcal{J}_5 \frac{\alpha^2 (\alpha^2 - 3\beta^2 \zeta)}{(\alpha^2 + \beta^2 \zeta)^3} - \frac{D}{\zeta} \left(\frac{T}{\Theta}\right)^2 \left(\frac{4\pi^2}{3} \mathcal{J}_5 + \frac{1}{2} \mathcal{J}_7\right) \frac{\beta^2 \zeta (3\alpha^2 - \beta^2 \zeta)}{(\alpha^2 + \beta^2 \zeta)^3} \right\} \frac{m^3 \zeta}{\hbar^3 \Lambda}, \quad (9)$$

$$\zeta Q = \frac{1}{3}\pi^2 (2m\zeta)^{\frac{1}{2}} \frac{\alpha (3\alpha^2 + \beta^2 \zeta)}{(\alpha^2 + \beta^2 \zeta)^2} - \frac{1}{2} \left(\frac{T}{\Theta}\right)^3 \left\{ \mathcal{J}_5 \frac{2\alpha \beta \zeta^{\frac{1}{2}} (3\alpha^2 - \beta^2 \zeta)}{(\alpha^2 + \beta^2 \zeta)^3} + \frac{D}{\zeta} \left(\frac{T}{\Theta}\right)^2 \left(\frac{4\pi^2}{3} \mathcal{J}_5 + \frac{1}{2} \mathcal{J}_7\right) \frac{2\alpha \beta \zeta^{\frac{1}{2}} (\alpha^2 - 3\beta^2 \zeta)}{(\alpha^2 + \beta^2 \zeta)^3} \right\} \frac{m^3 \zeta}{\hbar^3 \Lambda}. \quad (10)$$

3.3. Strong magnetic fields.

$$\zeta P = \frac{1}{\alpha^2} \left\{ \frac{2\pi^2}{3} (2m\zeta)^{\frac{1}{2}} \beta \zeta^{\frac{1}{2}} + \left(\frac{T}{\Theta}\right)^3 \mathcal{J}_5 \frac{m^3 \zeta}{\hbar^3 \Lambda} \right\}, \quad \zeta Q = \frac{\pi^2}{2\alpha} (2m\zeta)^{\frac{1}{2}}. \quad (11)$$

* The reader is reminded that $\alpha = eH/\hbar c$, that β is a constant determining the effect of the impurities (in the notation of Wilson (1937), $\beta = (2m)^{\frac{1}{2}} M/4\hbar^3$), and that D and Λ are constants determining the resistance of the pure metal.

4. THE THERMOELECTRIC POWER

4.1. *Single-band model.* At high temperatures a time of relaxation exists, and the thermoelectric power in a magnetic field of arbitrary magnitude can readily be calculated by means of equation (1) together with (8) and I (27), (28). The resulting expression is complicated, and owing to its restricted validity it will not be considered further here. It is of greater interest to consider the possibility of setting up an interpolation formula, analogous to the expressions obtained in I, which can be used for all temperatures and magnetic fields. By analogy with the procedure in I, §§ 4 and 6, such a formula would be expected to depend in some way on an interpolation formula for the thermoelectric power of a metal containing a single band, corresponding to I, equations (54) and (73) for the electrical and thermal conductivities. No such formula has so far been given, and it is therefore necessary to begin by supplying it here. The formula is obtained by writing down the exact expressions for $\mathfrak{S}$ in the three limiting cases where the solution is known, and guessing a generalized expression which reduces to the correct form in these limiting cases.

At high temperatures it is found, using (1), (suppressing all terms referring to the d -band and omitting the suffix s), together with (8), I (27), (28) and the expression (Wilson 1936, pp. 208, 223*)

$$\frac{1}{\tau} = \frac{\hbar\beta\zeta^{\frac{1}{2}}}{m} + \frac{(2m)^{\frac{1}{2}} D T}{4\hbar^2\zeta^{\frac{1}{2}}\Lambda \Theta} \quad (12)$$

for the time of relaxation, that

$$\mathfrak{S} = \frac{\pi^2 k^2 T}{3\zeta} \frac{1 + \frac{3(2m)^{\frac{1}{2}} D T}{8\hbar^3 \Lambda \beta \zeta^{\frac{3}{2}} \Theta}}{1 + \frac{(2m)^{\frac{1}{2}} D T}{8\hbar^3 \Lambda \beta \zeta^{\frac{3}{2}} \Theta}}. \quad (13)$$

At low temperatures the corresponding expression is

$$\mathfrak{S} = \frac{\pi^2 k^2 T}{3\zeta} \left\{ 1 + \frac{(2m)^{\frac{1}{2}} D}{4\hbar^3 \Lambda \beta \zeta^{\frac{3}{2}}} \left(\frac{T}{\Theta} \right)^5 \left(4\mathcal{J}_5 - \frac{1}{2\pi^2} \mathcal{J}_7 \frac{\alpha^2 - \beta^2 \zeta}{\alpha^2 + \beta^2 \zeta} \right) \right\}, \quad (14)$$

which is a remarkable result since it shows an explicit dependence of $\mathfrak{S}$ on the magnetic field, due to the non-existence of a time of relaxation at low temperatures. This question is considered further below.

For an infinitely large magnetic field, finally,

$$\mathfrak{S} = \frac{\pi^2 k^2 T}{3\zeta} \frac{1 + \frac{3(2m)^{\frac{1}{2}}}{4\pi^2 \hbar^3 \Lambda \beta \zeta} \left(\frac{T}{\Theta} \right)^3 \left\{ \mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta} \right)^2 (2\pi^2 \mathcal{J}_5 - \frac{1}{2} \mathcal{J}_7) \right\}}{1 + \frac{3(2m)^{\frac{1}{2}}}{4\pi^2 \hbar^3 \Lambda \beta \zeta} \left(\frac{T}{\Theta} \right)^3 \left\{ \mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta} \right)^2 \left(\frac{2\pi^2}{3} \mathcal{J}_5 - \frac{1}{2} \mathcal{J}_7 \right) \right\}}. \quad (15)$$

Now consider the expression

$$\mathfrak{S} = \frac{\pi^2 k^2 T}{3\zeta} \frac{1 + \frac{3(2m)^{\frac{1}{2}}}{4\pi^2 \hbar^3 \Lambda \beta \zeta} \left(\frac{T}{\Theta} \right)^3 \left\{ \mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta} \right)^2 \left(2\pi^2 \mathcal{J}_5 - \frac{1}{2} \mathcal{J}_7 \frac{H^2 - (n\epsilon\epsilon\rho_0)^2}{H^2 + (n\epsilon\epsilon\rho_0)^2} \right) \right\}}{1 + \frac{3(2m)^{\frac{1}{2}}}{4\pi^2 \hbar^3 \Lambda \beta \zeta} \left(\frac{T}{\Theta} \right)^3 \left\{ \mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta} \right)^2 \left(\frac{2\pi^2}{3} \mathcal{J}_5 - \frac{1}{2} \mathcal{J}_7 \frac{H^2 - (n\epsilon\epsilon\rho_0)^2}{H^2 + (n\epsilon\epsilon\rho_0)^2} \right) \right\}}. \quad (16)$$

* Wilson's notation differs considerably from the one used here.

where $n = (2m\zeta)^{1/3}/(3\pi^2\hbar^3)$ is the number of electrons per unit volume, and where

$$\frac{1}{\sigma_0} = \rho_0 = \frac{3\pi^2\hbar^4\beta}{(2m)^{1/3}\epsilon^2\zeta} + \frac{3\pi^2\hbar D}{2\epsilon^2\zeta^3\Lambda} \left(\frac{T}{\Theta}\right)^5 \mathcal{J}_5 \quad (17)$$

is the usual interpolation formula for the electrical resistivity of a metal containing a single band. It is seen at once that (16) reduces to (15) when H is infinite. At low temperatures all terms involving $\mathcal{J}_6$ and $\mathcal{J}_7$ may be treated as small, and (14) is then obtained as the first approximation. At high temperatures, finally,

$$(n-1)\mathcal{J}_n \simeq (\Theta/T)^{n-1},$$

and (13) is obtained on neglecting terms of order $(\Theta/T)^2$ compared with the leading term. Thus equation (16) may be adopted as the interpolation formula for the thermoelectric power of a metal containing a single band.

The corresponding formula for the adiabatic Ettingshausen-Nernst coefficient will also be required. It can be established by similar methods, and it is found that

$$\begin{aligned} \frac{1}{B_{EN}^q} = & -\frac{2}{3}nc\zeta \left[\frac{9\hbar^4\beta}{(2m)^{1/3}\zeta k^2 T} + \frac{27\hbar}{4\pi^2\zeta^2 k^2 \Lambda \Theta} \left(\frac{T}{\Theta}\right)^2 \right. \\ & \left. \times \left(\mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta}\right)^2 \left(\frac{2\pi^2}{3} \mathcal{J}_5 - \frac{1}{5} \mathcal{J}_7 \frac{3H^2 + (nec\rho_0)^2}{H^2 + (nec\rho_0)^2} \right) \right) \right]. \quad (18) \end{aligned}$$

While the interpolation formulae for σ and κ when $H = 0$ are identical with the exact expressions for $H = \infty$ (Kohler 1940, 1941c), equation (16) shows that this is no longer true for $\mathfrak{S}$. It is, however, known from Kohler's results for $H = \infty$ and Dube's results for $H = 0$ (Dube 1938) that the free electron model does lead to finite magneto-resistance effects if the calculations are pushed to a higher degree of approximation than is considered in the present work. In the case of the thermoelectric power a corresponding effect shows up in the first approximation, and has therefore to be included in the interpolation formula for $\mathfrak{S}$. However, the magnetic change predicted by (16) is small and is not in accordance with the experimental facts, and is of little importance compared with the effects to be discussed below in connexion with the two-band model.

4.11. *Interpolation formulae for P and Q .* The simplest way of obtaining the corresponding generalized expressions for the two-band model is to set up the interpolation formulae for P and Q . To do this it is only necessary to choose P and Q in such a way that equations (1) and (5) lead to (16) and (18), considering a single band and using the interpolation formulae I, (55), (56), (71), (72) for V, W, X, Y . These conditions are sufficient to determine P and Q . They lead to two linear equations expressing $\mathfrak{S}$ and B_{EN}^q in terms of P and Q , which, when solved, give

$$P = \frac{\pi^2(2m\zeta)^{1/3}n}{3\hbar\kappa_0} \frac{\left(\frac{n\epsilon^2\rho_0 n\epsilon^2 L_n T}{\hbar} - \alpha^2\right) \mathfrak{S} - \alpha^2 \left(\frac{n\epsilon^2\rho_0}{\hbar} + \frac{n\epsilon^2 L_n T}{\hbar\kappa_0}\right) \hbar c B_{EN}^q}{\left(\alpha^2 + \frac{n^2\epsilon^4\rho_0^2}{\hbar^2}\right) \left(\alpha^2 + \frac{n^2\epsilon^4 L_n^2 T^2}{\hbar^2\kappa_0^2}\right)}, \quad (19)$$

$$Q = \alpha \frac{\pi^2 (2m\zeta)^{\frac{1}{2}} n}{3\hbar\kappa_0} \frac{\left(\frac{n\epsilon^2 \rho_0}{\hbar} \frac{n\epsilon^2 L_n T}{\hbar\kappa_0} - \alpha^2 \right) \hbar c B_{EN}^2 + \left(\frac{n\epsilon^2 \rho_0}{\hbar} + \frac{n\epsilon^2 L_n T}{\hbar\kappa_0} \right) \mathfrak{S}}{\left(\alpha^2 + \frac{n^2 \epsilon^4 \rho_0^2}{\hbar^2} \right) \left(\alpha^2 + \frac{n^2 \epsilon^4 L_n^2 T^2}{\hbar^2 \kappa_0^2} \right)}, \quad (20)$$

where $L_n = \frac{1}{2}(\pi\hbar/\epsilon)^2$, $\mathfrak{S}$ is given by (16), ρ_0 by (17), B_{EN}^2 by (18), and

$$\frac{1}{\kappa_0} = \frac{9\hbar^4 \beta}{(2m)^{\frac{1}{2}} \zeta k^2 T} + \frac{27\hbar}{4\pi^2 \zeta^2 k^2 \Lambda \Theta} \left(\frac{T}{\Theta} \right)^2 \left\{ \mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta} \right)^2 \left(\frac{2\pi^2}{3} \mathcal{J}_5 - \frac{1}{2} \mathcal{J}_7 \right) \right\}. \quad (21)$$

As a check it can be verified by means of elementary calculations, which will not be reproduced here, that (19) and (20) reduce to (8) at high temperatures, to (9) and (10) at low temperatures and to (11) for very large magnetic fields.

A complete set of interpolation formulae for V , W , X , Y , P , Q is now available, and can be used in conjunction with equations (1) to (7) to derive generalized expressions for all the galvano- and thermomagnetic effects.

4.2. *Two-band model.* The values of $\mathfrak{S}$ and B_{EN}^2 for the s -band alone but in an arbitrary magnetic field are given by expressions like (16) and (18) but with the suffix s inserted where necessary, and will be denoted by $\mathfrak{S}_s$ and $B_{EN,s}^2$ respectively; also, $\mathfrak{S}_{0s}$ and $B_{EN,0s}^2$ are used to denote the values of $\mathfrak{S}_s$ and $B_{EN,s}^2$ when $H = 0$. In writing down the corresponding expressions for the d -band, it must be borne in mind that $\mathfrak{S}_s$ and $\mathfrak{S}_d$ have opposite signs while $B_{EN,s}^2$ and $B_{EN,d}^2$ have the same sign, as is shown by equations (1) and (5). By means of equation (1) together with (19), (20) and I, (55), (56), (71), (72) it is found, after much rearrangement and simplification, that, for the most general case of two overlapping bands,

$$\begin{aligned} \mathfrak{S} &= \left\{ (\sigma_{0s} + \sigma_{0d})^2 + \left(\frac{H}{\epsilon c} \right)^2 \frac{(n_s - n_d)^2}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right\} \left\{ \kappa_{0s} + \kappa_{0d} + \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right)^2 \left(\frac{\kappa_{0s}}{n_s^2} + \frac{\kappa_{0d}}{n_d^2} \right) \kappa_{0s} \kappa_{0d} \right\} \\ &= n_s^2 \frac{\mathfrak{S}_s}{\kappa_{0s}} \left\{ \frac{\sigma_{0s}}{n_s} (\sigma_{0s} + \sigma_{0d}) + \left(\frac{H}{\epsilon c} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right\} \left\{ \frac{\kappa_{0s}}{n_s} (\kappa_{0s} + \kappa_{0d}) + \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \kappa_{0s}^2 \kappa_{0d}^2 \right\} \\ &\quad + n_d^2 \frac{\mathfrak{S}_d}{\kappa_{0d}} \left\{ \frac{\sigma_{0d}}{n_d} (\sigma_{0s} + \sigma_{0d}) - \left(\frac{H}{\epsilon c} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right\} \left\{ \frac{\kappa_{0d}}{n_d} (\kappa_{0s} + \kappa_{0d}) - \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \kappa_{0s}^2 \kappa_{0d}^2 \right\} \\ &\quad - \left(\frac{H}{\epsilon c} \right) \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right) \left(\frac{\mathfrak{S}_s}{\kappa_{0s}} + \frac{\mathfrak{S}_d}{\kappa_{0d}} \right) \left(\frac{\sigma_{0s}}{n_s} + \frac{\sigma_{0d}}{n_d} \right) \left(\frac{\kappa_{0s}}{n_s} + \frac{\kappa_{0d}}{n_d} \right) \sigma_{0s} \sigma_{0d} \kappa_{0s} \kappa_{0d} \\ &\quad - \frac{1}{c} H^2 n_s \frac{B_{EN,s}^2}{\kappa_{0s}} \left[\left(\frac{\sigma_{0s}}{n_s} + \frac{\sigma_{0d}}{n_d} \right) \left(\frac{\kappa_{0s}}{n_s} (\kappa_{0s} + \kappa_{0d}) + \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \kappa_{0s}^2 \kappa_{0d}^2 \right) \sigma_{0s} \sigma_{0d} \right. \\ &\quad \left. + \frac{3\epsilon^2}{\pi^2 k^2 T} \left(\frac{\kappa_{0s}}{n_s} + \frac{\kappa_{0d}}{n_d} \right) \left\{ \frac{\sigma_{0s}}{n_s} (\sigma_{0s} + \sigma_{0d}) + \left(\frac{H}{\epsilon c} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right\} \kappa_{0s} \kappa_{0d} \right] \\ &\quad + \frac{1}{c} H^2 n_d \frac{B_{EN,d}^2}{\kappa_{0d}} \left[\left(\frac{\sigma_{0s}}{n_s} + \frac{\sigma_{0d}}{n_d} \right) \left(\frac{\kappa_{0d}}{n_d} (\kappa_{0s} + \kappa_{0d}) - \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \kappa_{0s}^2 \kappa_{0d}^2 \right) \sigma_{0s} \sigma_{0d} \right. \\ &\quad \left. + \frac{3\epsilon^2}{\pi^2 k^2 T} \left(\frac{\kappa_{0s}}{n_s} + \frac{\kappa_{0d}}{n_d} \right) \left\{ \frac{\sigma_{0d}}{n_d} (\sigma_{0s} + \sigma_{0d}) - \left(\frac{H}{\epsilon c} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right\} \kappa_{0s} \kappa_{0d} \right], \quad (22) \end{aligned}$$

$\sigma_{0s}, \sigma_{0d}, \kappa_{0s}, \kappa_{0d}$ being given by equations like (17) and (21) but with the suffix s or d inserted where necessary. In the absence of a magnetic field this reduces to

$$\mathfrak{S}_0 = \frac{\sigma_{0s} \mathfrak{S}_{0s} + \sigma_{0d} \mathfrak{S}_{0d}}{\sigma_{0s} + \sigma_{0d}}. \quad (23)$$

4.21. Equations (22) and (23) make it possible to work out the variation of the thermoelectric power with the magnetic field and the temperature in any particular case. To get a general idea of the results, various assumptions are introduced which help to simplify (22) considerably. In the first place, the variation with H of $\mathfrak{S}_s, \mathfrak{S}_d, B_{EN,s}^q$ and $B_{EN,d}^q$ is neglected, since it is unimportant compared with the effect due to the two-band model, and these quantities are therefore replaced by their values for $H = 0$. It is also assumed that $\sigma_{0s} = \sigma_{0d} = \frac{1}{2}\sigma_0$, $\kappa_{0s} = \kappa_{0d} = \frac{1}{2}\kappa_0$, $B_{EN,0s}^q = B_{EN,0d}^q$, and $\mathfrak{S}_{0s} = -\mathfrak{S}_{0d}/\lambda$. There are two cases to consider according as n_s is or is not equal to n_d , but, since there does not appear to be any essential difference between the two cases, the discussion will here be confined to the simpler case where $n_s = n_d = \frac{1}{2}n$. In this case $\mathfrak{S}_0 = \frac{1}{2}(1 - \lambda) \mathfrak{S}_{0s}$, and

$$\mathfrak{S} = \mathfrak{S}_0 \frac{1 - \frac{3H^2}{\pi^2 k^2 n^2 c^2 T} \sigma_0 \kappa_0}{1 + \left(\frac{3H\epsilon}{\pi^2 k^2 n c T} \right)^2 \kappa_0^2}. \quad (24)$$

This may be written in the form

$$\mathfrak{S} = \mathfrak{S}_0 \frac{1 - \left(\frac{H}{n\epsilon c \rho_0} \right)^2 \frac{L_0}{L_n}}{1 + \left(\frac{H}{n\epsilon c \rho_0} \right)^2 \frac{L_0^2}{L_n^2}}, \quad (25)$$

where $L_n = \frac{1}{3}(\pi k/\epsilon)^2$ and $L_0 = \kappa_0/\sigma_0 T$, as in I, § 6.2.

Thus, if $\mathfrak{S}_0$ is positive, $\mathfrak{S}$ decreases steadily as H increases, changes sign for a certain value of H , and in very strong fields it approaches the saturation value

$$\mathfrak{S}_{H \rightarrow \infty} = -\frac{L_n}{L_0} \mathfrak{S}_0, \quad (26)$$

which is, in general, greater than $\mathfrak{S}_0$ in absolute value* (Makinson 1938). If $\mathfrak{S}_0$ is negative, however, $\mathfrak{S}$ increases as H increases and eventually becomes positive.

The change in the thermoelectric power is $-\Delta\mathfrak{S}/\epsilon$, where

$$\Delta\mathfrak{S} = \mathfrak{S} - \mathfrak{S}_0 = -\mathfrak{S}_0 \frac{\left(\frac{H}{n\epsilon c \rho_0} \right)^2 \frac{L_0}{L_n} \left(1 + \frac{L_0}{L_n} \right)}{1 + \left(\frac{H}{n\epsilon c \rho_0} \right)^2 \frac{L_0^2}{L_n^2}}. \quad (27)$$

At very low temperatures $L_0 = L_n$, $\rho_0 = \rho_r$ (the residual resistance) and $\mathfrak{S}_0$ is proportional to T . Hence $\Delta\mathfrak{S} = 0$ when $T = 0$, and for small values of T it is proportional to T . At high temperatures $L_0 = L_n$, and $\mathfrak{S}_0$ and ρ_0 are both proportional to T , so

* Equation (22) shows that there is saturation in strong fields also when $n_s \neq n_d$, but the details of the field variation will be more complicated.

that $\Delta\mathcal{S}$ tends to zero like T^{-1} as T tends to infinity. In fact, with the magnetic fields that are obtainable in practice, $ne\epsilon\rho_0 \gg H$ at room temperature for normal metals, so that $\Delta\mathcal{S} \ll \mathcal{S}_0$ according to (27), which means that the change in thermoelectric power will, in general, be too small to be detected at room temperature.

Thus $\Delta\mathcal{S}$ is very small at very low and high temperatures, and must therefore pass through a maximum (in absolute value) at some intermediate value of T . For a more detailed discussion it is sufficient to make the further assumptions that $L_0 = L_n$ and that $\mathcal{S}_0$ is proportional to T for all temperatures.* Equation (27) then leads to the following condition for the maximum of $|\Delta\mathcal{S}|$:

$$H = \left(\frac{2T}{\rho_0} \frac{d\rho_0}{dT} - 1 \right)^{\frac{1}{2}} ne\epsilon\rho_0. \quad (28)$$

Now ρ_0 can never be less than ρ_r ; hence, when $H = 0$, (28) is satisfied for that temperature for which $\frac{2T}{\rho_0} \frac{d\rho_0}{dT} = 1$, that is, for which ρ_0 is proportional to $\sqrt{T}$ over a small temperature range. This temperature lies in the region where the residual and ideal resistances are of the same order of magnitude (for very pure metals this means temperatures of the order of 10°K). As H increases, this condition continues to hold approximately until H is of the order of $ne\epsilon\rho_r$; as H increases further, the condition for the maximum is that H and $ne\epsilon\rho_0$ must be of the same order of magnitude (since $\frac{2T}{\rho_0} \frac{d\rho_0}{dT} - 1$ is always of order unity), and hence the temperature of the maximum increases with H .

The qualitative behaviour of $|\Delta\mathcal{S}|$ as a function of temperature is therefore as follows. $|\Delta\mathcal{S}|$ is very small at sufficiently high temperatures, rises to a maximum as the temperature decreases and then tends to zero as T approaches zero (linearly for sufficiently small T). For small values of the magnetic field, the maximum occurs at a temperature of the order of 10°K . As H increases, $|\Delta\mathcal{S}|$ increases, but the temperature at which the maximum occurs remains approximately constant until H is of the order of $ne\epsilon\rho_r$; for larger values of H , the temperature of the maximum increases with H (linearly for sufficiently large H).

4.3. Beryllium appears to be the only metal (apart from the metals of the abnormal bismuth group) for which there are any experimental results (Grüneisen & Erfling 1939). The change in thermoelectric power is too small to be detected at temperatures above about 150°K ; as lower temperatures it rises to a maximum and then decreases towards zero as T tends to zero. The position of the maximum moves towards higher temperatures as the magnetic field increases. These results are in qualitative agreement with the predictions of the two-band model, but it must still be verified that there is also order-of-magnitude quantitative agreement. For one

* In general, L_0 is less than L_n (Makinson 1938); also $\mathcal{S}_0$ is given by (16), (with $H = 0$), and is a linear function of T only at very high and very low temperatures. Taking into account the exact temperature variation of L_0 and $\mathcal{S}_0$ changes the quantitative but not the qualitative nature of the results.

of the specimens investigated, the maximum was found to occur at 60° K in a field of 12,200 gauss. At this temperature the resistivity of the specimen is about 3×10^{-20} gaussian units, and (28) therefore indicates that n is of the order of 3×10^{22} , which agrees in order of magnitude with the value derived from the magneto-resistance effects in I, § 6.2. The maximum change in the thermoelectric power is observed to be of the same order of magnitude as the thermoelectric power in the absence of a magnetic field, which agrees with (27) and (28).

5. THE TRANSVERSE EFFECTS IN ZERO MAGNETIC FIELD

5.1. *Single-band model with a time of relaxation.* When a time of relaxation exists, the coefficients of the transverse effects are readily calculated by means of equations (3) to (7) together with (8) and I, (27), (28). For the present only the case of a vanishingly small magnetic field will be considered, the question of the influence of H being left until § 6. The formulae for the simplest model of perfectly free electrons are obtained by suppressing all terms referring to the d -band in equations (3) to (7); omitting also the suffix s , it is found that

$$A_H = -\frac{1}{nec}, \quad (29)$$

$$B_{RL} = -\frac{e\tau}{mc}, \quad (30)$$

$$B_{EN}^t = \frac{\pi^2 k^2 T}{3mc} \frac{\partial \tau}{\partial \zeta}, * \quad (31)$$

$$A_E = \frac{T}{nec\tau} \frac{\partial \tau}{\partial \zeta}, \quad (32)$$

τ being regarded as an arbitrary function of ζ . Analogous formulae hold for a metal containing a single d -band, except that e has to be replaced by $-e$, so that A_H and B_{RL} are positive instead of negative.

Combining (29) and (30) and using the expression (Wilson 1936, p. 161)

$$\sigma = \frac{nec^2\tau}{m} \quad (33)$$

for the electrical conductivity, it is found that

$$B_{RL} = A_H \sigma. \quad (34)$$

Also, introducing $A_{EN} = B_{EN}/\kappa = 3mB_{EN}/(\pi^2 k^2 n T \tau)$, (31) and (32) lead to

$$A_{EN}^t = \frac{A_E}{T}, \quad (35)$$

and, combining (34) and (35) and introducing $A_{RL} = B_{RL}/\kappa$, it is found that

$$\frac{A_H A_{EN}^t}{A_E A_{RL}} = \frac{\pi^2}{3} \left(\frac{k}{e} \right)^2. \quad (36)$$

* It will be recalled that B_{EN}^t is taken to represent the measured value of the Ettingshausen-Nernst coefficient (see § 2).

The relations (34), (35) and (36) have been known for a long time (Bridgman 1924), and Meissner (1935, p. 383) has shown that there is order-of-magnitude agreement with the experimental values for room temperature. The experimental evidence is considered further in § 7.2.

Equations (29) to (32) have been discussed by Sommerfeld & Frank (1931) in the special case where the free path is independent of ζ (and therefore τ is proportional to ζ^{-1}); the generalization for the case where τ is an arbitrary function of ζ is due to Kohler (1941*a*). The Sommerfeld & Frank case is realized at extremely low temperatures, where the effect of the impurities is dominant; at high temperatures, however, τ is proportional to $\zeta^{\frac{1}{2}}$ (Wilson 1936, pp. 208, 223; compare also equation (12) of the present paper). The formulae for the two limiting cases of very low and very high temperatures are thus obtained from (29) to (32) by replacing $\partial\tau/\partial\zeta$ by $-\frac{1}{2}\tau/\zeta$ and $\frac{3}{2}\tau/\zeta$ respectively. They are special cases of the generalized formulae given in § 5.2 and need not, therefore, be discussed separately.

5.2. *Single-band model: arbitrary temperature.* At intermediate temperatures it is not legitimate to assume that a time of relaxation exists, and equations (29) to (32) cannot be used. By means of the interpolation formulae I, (55), (56), (71), (72) for V, W, X, Y and (19), (20) of the present paper for P, Q it is possible, however, to calculate the generalized expressions which are approximately valid over the whole temperature-range. The equations which replace (29) to (32) are found to be

$$A_H = -\frac{1}{nec}, \quad (37)$$

$$B_{RL} = -\frac{3e\kappa_0}{\pi^2 k^2 n c T}, \quad (38)$$

$$B_{EN}^t = B_{EN,0}^t + \frac{3\kappa_0 \mathfrak{E}_0}{\pi^2 k^2 n c T}, \quad (39)$$

$$A_E = \frac{T B_{EN,0}^t}{\kappa_0} + \frac{3\mathfrak{E}_0}{\pi^2 k^2 n c}, \quad (40)$$

where κ_0 is given by (21), and $B_{EN,0}^t$ and $\mathfrak{E}_0$ are obtained by putting $H = 0$ in (18) and (16), that is,

$$\frac{1}{B_{EN,0}^t} = -\frac{2}{3}nc\zeta \left[\frac{9h^4\beta}{(2m)^{\frac{1}{2}}\zeta k^2 T} + \frac{27h}{4\pi^2\zeta^2 k^2 \Lambda \Theta} \left(\frac{T}{\Theta} \right)^2 \left\{ \mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta} \right)^2 \left(\frac{2\pi^2}{3} \mathcal{J}_5 - \frac{1}{2} \mathcal{J}_7 \right) \right\} \right], \quad (41)$$

$$\mathfrak{E}_0 = \frac{\pi^2 k^2 T}{3\zeta} \frac{1 + \frac{3(2m)^{\frac{1}{2}}}{4\pi^2 h^3 \Lambda \beta \zeta} \left(\frac{T}{\Theta} \right)^3 \left\{ \mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta} \right)^2 \left(\frac{2\pi^2}{3} \mathcal{J}_5 + \frac{1}{2} \mathcal{J}_7 \right) \right\}}{1 + \frac{3(2m)^{\frac{1}{2}}}{4\pi^2 h^3 \Lambda \beta \zeta} \left(\frac{T}{\Theta} \right)^3 \left\{ \mathcal{J}_5 + \frac{D}{\zeta} \left(\frac{T}{\Theta} \right)^2 \left(\frac{2\pi^2}{3} \mathcal{J}_5 + \frac{1}{2} \mathcal{J}_7 \right) \right\}}. \quad (42)$$

It is now possible to discuss the predictions of the free electron model for the temperature variation of the coefficients over the whole temperature range.

Equation (37) shows that the well-known formula for the Hall coefficient is of general validity as an interpolation formula (as was to be expected since it does not

involve the time of relaxation). A_H should therefore be independent of T for all temperatures, which is roughly in accord with the experimental results for many normal metals (but see §§ 5.3 and 7.3 *infra*).

The temperature variation of κ_0 has been discussed by Makinson (1938). κ_0 is independent of T at high temperatures, rises to a maximum at very low temperatures and then tends to zero as T approaches zero (linearly for sufficiently small T). Hence, according to (38), B_{RL} is proportional to T^{-1} at high temperatures, but increases more rapidly than T^{-1} at low temperatures; finally, when the effect of the impurities is dominant, B_{RL} tends to a constant value $-(nec\rho_r)^{-1}$, where ρ_r is the residual resistance. The alternative coefficient $A_{RL} = B_{RL}/\kappa_0$ is proportional to T^{-1} for all T .

Comparison of equations (21) and (41) shows that the expressions for $-3\kappa_0/(2nc\zeta)$ and $B_{EN,0}^i$ are very similar, the only difference arising from the term in $\mathcal{J}_7$ which is negligible except for temperatures close to the Debye temperature. For a qualitative discussion it will be sufficient to put $B_{EN,0}^i = -3\kappa_0/(2nc\zeta)$.^{*} Further, (42) shows that it is possible to write $\mathfrak{S}_0 = x\pi^2k^2T/\zeta$, where x decreases steadily from the value 1 at high temperatures to the value $\frac{1}{2}$ at very low temperatures.

Equations (39) and (40) now reduce to

$$B_{EN}^i = \frac{3\kappa_0}{nc\zeta} \left(x - \frac{1}{2}\right), \quad (43)$$

$$A_E = \frac{3T}{nc\zeta} \left(x - \frac{1}{2}\right). \quad (44)$$

At high temperatures $x = 1$ and κ_0 is independent of T , so that B_{EN}^i is positive and independent of T , while A_E is positive and proportional to T . As T decreases, B_{EN}^i and A_E both decrease and become zero at that temperature for which $x = \frac{1}{2}$. At extremely low temperatures $x = \frac{1}{2}$ and κ_0 is proportional to T ; hence, as x decreases below the value $\frac{1}{2}$, B_{EN}^i and A_E become negative, pass through a minimum and finally tend to zero as T approaches zero (linearly for sufficiently small T). The minimum occurs in the temperature region where the residual and ideal resistivities are of the same order of magnitude.

The experimental results for the temperature variation of the coefficients are very meagre and always refer to high temperatures (except for the Hall coefficient); they are considered further in § 7.4. Measurements at low temperatures are essential for a complete experimental test of the behaviour predicted by the free electron model.

It is easily seen from equations (37) to (40) that the relations (35) and (36) among the coefficients remain valid for all temperatures, but that (34) must, in the general case, be replaced by

$$B_{RL} = \frac{L_0}{L_n} A_H \sigma_0. \quad (45)$$

^{*} This relation is actually exact when H is infinite (since equations (18) and (21) are exact when H is infinite).

where σ_0 is given by (17). At sufficiently high temperatures $L_0 = L_n$, but for normal metals L_0/L_n may be considerably less than unity over an extended temperature range (compare Makinson 1938, figure 3. Note that his notation differs slightly from ours). The experimental evidence relating to equation (45) is discussed in § 7.2.

5.3. *Two-band model.* It is now of interest to investigate to what extent the results obtained above for a metal containing a single band are modified in the more general case of two overlapping bands. It will be found that, although the single-band model gives the right order of magnitude for the transverse effects, its more detailed predictions regarding the temperature variation and inter-relation of the coefficients (especially as regards the low temperature behaviour) cannot be expected to hold for real metals except in special cases, and attempts to explain the experimental facts on the basis of this model are not, in general, likely to be successful.

Retaining the terms which refer to the d -band in the formal expressions (3) to (7), it is found that the equations which replace (37) to (40) are

$$A_H = -\frac{1}{\epsilon c} \frac{\frac{\sigma_{0s}^2}{n_s} - \frac{\sigma_{0d}^2}{n_d}}{(\sigma_{0s} + \sigma_{0d})^2}, \quad (46)$$

$$B_{RL} = -\frac{3\epsilon}{\pi^2 k^2 c T} \frac{\frac{\kappa_{0s}^2}{n_s} - \frac{\kappa_{0d}^2}{n_d}}{\kappa_{0s} + \kappa_{0d}}, \quad (47)$$

$$B_{EN}^t = \frac{1}{\sigma_{0s} + \sigma_{0d}} \left\{ \sigma_{0s} B_{EN,0s}^q + \sigma_{0d} B_{EN,0d}^q + \frac{3}{\pi^2 k^2 c T} \left(\frac{\sigma_{0s} \kappa_{0s} \mathfrak{S}_{0s}}{n_s} - \frac{\sigma_{0d} \kappa_{0d} \mathfrak{S}_{0d}}{n_d} \right) \right. \\ \left. + \frac{1}{\epsilon^2 c} \frac{\sigma_{0s} \sigma_{0d}}{(\sigma_{0s} + \sigma_{0d})^2} \left(\frac{\sigma_{0s}}{n_s} + \frac{\sigma_{0d}}{n_d} \right) (\mathfrak{S}_{0s} - \mathfrak{S}_{0d}) \right\}, \quad (48)$$

$$A_E = \frac{1}{(\sigma_{0s} + \sigma_{0d})(\kappa_{0s} + \kappa_{0d})} \left\{ T(\sigma_{0s} B_{EN,0s}^q + \sigma_{0d} B_{EN,0d}^q) + \frac{3}{\pi^2 k^2 c} \left(\frac{\sigma_{0s} \kappa_{0s} \mathfrak{S}_{0s}}{n_s} - \frac{\sigma_{0d} \kappa_{0d} \mathfrak{S}_{0d}}{n_d} \right) \right. \\ \left. + \frac{T}{\epsilon^2 c} \frac{\sigma_{0s} \sigma_{0d}}{(\sigma_{0s} + \sigma_{0d})^2} \left(\frac{\sigma_{0s}}{n_s} + \frac{\sigma_{0d}}{n_d} \right) \frac{\mathfrak{S}_{0s} - \mathfrak{S}_{0d}}{\kappa_{0s} + \kappa_{0d}} \right\}, \quad (49)$$

the notation being the same as in § 4.2.

These equations show that A_H and B_{RL} are negative or positive according as the conduction is predominantly due to the s -band or the d -band. B_{EN}^t and A_E are, however, always positive at high temperatures, the s - and d -bands giving contributions of the same sign. This is due to the fact that, while A_H and B_{RL} are odd functions of the electronic charge e , B_{EN} and A_E are even functions of e , so that conduction by 'positive holes' does not lead to anomalous effects in the latter case. There are, however, many metals, including the monovalent metals Cu, Ag, Au, which have negative Ettingshausen and Ettingshausen-Nernst coefficients at high temperatures. This is clearly a more complicated effect than the occurrence of the positive Hall and Righi-Leduc coefficients, and some more general model than those so far considered would be necessary for its elucidation. The type of model required is indicated by equations (31) and (32), which show that B_{EN}^t and A_E are proportional

to the energy derivative of the time of relaxation, and are therefore negative provided that τ is a decreasing function of the energy at the surface of the Fermi distribution.* No model which has this property at high temperatures has so far been proposed; in addition to giving negative values for B_{EN}^i and A_E , it would presumably explain the positive thermoelectric powers of Cu, Ag and Au.

5.31. The temperature variation of the coefficients predicted by equations (46) to (49) is, in general, more complicated than that predicted by the single-band model.

Writing $\sigma_{os} = p\sigma_0$, $\sigma_{od} = (1-p)\sigma_0$, the expression (46) for the Hall coefficient becomes

$$A_H = -\frac{1}{ec} \left\{ \frac{p^2}{n_s} - \frac{(1-p)^2}{n_d} \right\}. \quad (50)$$

From (50) it follows that

$$\frac{\partial A_H}{\partial p} = -\frac{2}{ec} \left(\frac{p}{n_s} + \frac{1-p}{n_d} \right) < 0;$$

hence A_H is smaller (algebraically), the larger the value of p , i.e. the larger the proportion of the total electric current which is carried by the s -band. Temperature variations of A_H can be accounted for by allowing p to vary with the temperature, and such an argument has been used by Jones (1936) in his discussion of the Hall effect in bismuth. However, if one accepts equation (17) for the electrical conductivity, any temperature variation of p is unlikely to be very marked and should in any case set in only at very low temperatures where the residual and ideal resistivities are of the same order of magnitude. The present model might therefore be used, at best, to explain a change in A_H by a factor of (say) 2 at very low temperatures. Jones's argument requires a larger variation of p than seems reasonable according to the present considerations, and some other mechanism appears to be necessary to account for his assumptions.

The Hall coefficients of many normal metals increase in absolute value as the temperature is lowered, but become constant at extremely low temperatures. The experimental data are considered in detail in § 7.3.

Similar considerations as to A_H apply to B_{RL} , but here the temperature dependence predicted by the free electron model (equation (38)) is probably more important than any effects due to the two-band model, and no significant new effects are to be expected. Equation (38) is therefore probably of wider validity than its derivation would suggest, and may be regarded as an approximation formula for the temperature variation of the Righi-Leduc coefficient of all metals. The detailed behaviour of B_{RL} as a function of temperature is obtained from (38) and Makinson's (1938) discussion of the thermal conductivity; it has been considered qualitatively in § 5.2. Measurements on a variety of metals at low temperatures would be required to verify the general validity of equation (38).

* In deriving equations (31) and (32) it has been assumed that $\partial^2 E / \partial |\mathbf{k}|^2$ is positive. The more general criterion for anomalous values of B_{EN}^i and A_E is that $\frac{\partial}{\partial E} \left(\tau \frac{\partial^2 E}{\partial |\mathbf{k}|^2} \right)$ should be negative.

For a qualitative discussion of B_{EN}^i and A_E , it is sufficient to put $\sigma_{os} = \sigma_{od} = \frac{1}{2}\sigma_0$, $\kappa_{os} = \kappa_{od} = \frac{1}{2}\kappa_0$, $n_s B_{EN, os}^i = n_d B_{EN, od}^i = -3\kappa_0/(4c\zeta)$, and $\mathfrak{S}_{os} = -\mathfrak{S}_{od} = x\pi^2 k^2 T/\zeta$, where $\frac{1}{2} \leq x \leq 1$ (compare § 5.2). Writing also $L_n = \frac{1}{2}(\pi k/\varepsilon)^2$, $L_0 = \kappa_0/\sigma_0 T$, equations (48) and (49) reduce to

$$B_{EN}^i = \frac{3\kappa_0}{4c\zeta} \left(\frac{1}{n_s} + \frac{1}{n_d} \right) \left(x \frac{L_n}{L_0} + x - \frac{1}{2} \right), \quad (51)$$

$$A_E = \frac{3T}{4c\zeta} \left(\frac{1}{n_s} + \frac{1}{n_d} \right) \left(x \frac{L_n}{L_0} + x - \frac{1}{2} \right). \quad (52)$$

Apart from the fact that $\frac{1}{n}$ is replaced by $\frac{1}{4} \left(\frac{1}{n_s} + \frac{1}{n_d} \right)$, equations (51) and (52) differ from the corresponding equations (43) and (44) for free electrons in having the additional term xL_n/L_0 . The temperature variation of L_0 has been discussed by Makinson (1938; see also I, § 6.2). For normal metals L_0 is equal to L_n at both high and very low temperatures but may be considerably less at intermediate temperatures. For metals such as bismuth, however, which have an abnormally small number of free electrons, L_0 is in general greater than L_n at intermediate temperatures. At high temperatures, therefore, the sign and temperature variation of B_{EN}^i and A_E are the same as for free electrons, only the magnitude of the coefficients being different. The behaviour is, however, entirely different at low temperatures, where the free electron model predicts that B_{EN}^i and A_E change sign. Equations (51) and (52) show that B_{EN}^i and A_E are only negative when the condition

$$\frac{L_n}{L_0} < \frac{1}{2x} - 1 \quad (53)$$

is satisfied. Now $\frac{1}{2} \leq x \leq 1$, so that $-\frac{1}{2} \leq \frac{1}{2x} - 1 \leq \frac{1}{2}$; hence B_{EN}^i and A_E are positive at high and also at very low temperatures, where $L_0 = L_n$. Also (53) can never hold if $L_0 \leq L_n$, and therefore B_{EN}^i and A_E are always positive in this case. If $L_0 > L_n$, however, it is possible that B_{EN}^i and A_E may become negative in some intermediate temperature range. The detailed behaviour is, in general, complicated, but it can be worked out from (51) and (52) for any particular case.

Finally, equations (46) to (49) show that the simple relations (36) and (45) derived for free electrons are only valid for the two-band model in the special case where it is legitimate to assume that a time of relaxation exists (and where (45) reduces to (34)). Thus the theoretical predictions for free electrons appear to be generally valid at high temperatures, but cannot hold for multivalent metals at low temperatures except (at best) as order-of-magnitude relations. On the other hand, comparison of (48) and (49) shows that the relation (35) between the Ettingshausen-Nernst and the Ettingshausen coefficient continues to be valid for the two-band model at all temperatures, and is thus of a more general type than (36) and (45).

These results of the electron theory concerning the relations among the coefficients are in accordance with the thermodynamic arguments given by Meissner (1935,

p. 316). The three relations (34), (35) and (36) are derived there, but the argument leading to (34) and (36) involves certain assumptions which are equivalent to assuming the validity of the Wiedemann-Franz law. Now this law is known to be a consequence of the existence of a time of relaxation (Wilson 1936, p. 175; I, p. 451), and thus Meissner's derivation can only be valid for high temperatures. The derivation of (35), however, appears to involve purely thermodynamic arguments only, and this relation should therefore be a general property of all models at all temperatures. There are unfortunately no experimental results with which to check the validity of (35) at low temperatures; for the room temperature data regarding the relations among the coefficients, see § 7.2.

6. THE FIELD VARIATION OF THE TRANSVERSE EFFECTS

6.1. The free electron model leads to values for the coefficients of the transverse effects which are independent of H for all values of H (at most, there is a negligible effect of the type (18)).* This is because the field variation of the transverse effects, like the magneto-resistance effect, depends essentially upon an average of the departure of the energy surfaces from being a singly-connected set of spheres, and the two-band model is therefore the simplest model which can be expected to give results of the correct order of magnitude. The generalizations of equations (46) to (49) for the case of a magnetic field of arbitrary magnitude are readily found to be

$$A_H = -\frac{1}{\epsilon c} \frac{\frac{\sigma_{0s}^2}{n_s} - \frac{\sigma_{0d}^2}{n_d} + \left(\frac{H}{\epsilon c}\right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2}{(\sigma_{0s} + \sigma_{0d})^2 + \left(\frac{H}{\epsilon c}\right)^2 \frac{(n_s - n_d)^2}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2}, \quad (54)$$

$$B_{RL} = -\frac{3\epsilon}{\pi^2 k^2 c T} \frac{\frac{\kappa_{0s}^2}{n_s} - \frac{\kappa_{0d}^2}{n_d} + \left(\frac{3H\epsilon}{\pi^2 k^2 c T}\right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \kappa_{0s}^2 \kappa_{0d}^2}{\kappa_{0s} + \kappa_{0d} + \left(\frac{3H\epsilon}{\pi^2 k^2 c T}\right)^2 \left(\frac{\kappa_{0s}}{n_s^2} + \frac{\kappa_{0d}}{n_d^2}\right) \kappa_{0s} \kappa_{0d}}, \quad (55)$$

$$B_{EN}^t = \left[\left(\frac{\sigma_{0s}}{n_s} (\sigma_{0s} + \sigma_{0d}) + \left(\frac{H}{\epsilon c} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right) \left(\frac{3\kappa_{0s} \mathfrak{S}_s}{\pi^2 k^2 c T} + n_s B_{EN,s}^q \right) \right. \\ \left. + \frac{\sigma_{0s} \sigma_{0d}}{n_s \epsilon^2 c} \left(\frac{\sigma_{0s}}{n_s} + \frac{\sigma_{0d}}{n_d} \right) \left(n_s \mathfrak{S}_s - \frac{3\epsilon^2 H^2 \kappa_{0s} B_{EN,s}^q}{\pi^2 k^2 c T} \right) \right] \left[1 + \left(\frac{3H\epsilon}{\pi^2 k^2 n_s c T} \right)^2 \kappa_{0s}^2 \right]^{-1} \\ \times \left[(\sigma_{0s} + \sigma_{0d})^2 + \left(\frac{H}{\epsilon c} \right)^2 \frac{(n_s - n_d)^2}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right]^{-1}$$

+ a similar term with s and d interchanged and the sign of $\mathfrak{S}$ changed, (56)

* This is actually true only for effects measured under adiabatic conditions. The isothermal effects for free electrons in general depend explicitly on H even when a time of relaxation exists (Kohler 1941a). Thus, for example, formula (56) for B_{EN}^t does not become independent of H on putting $n_s = 0$ or $n_d = 0$. Even here, however, the major part of the field variation is due to the departure of the energy surfaces from being a singly-connected set of spheres, and the predictions of the free electron model cannot be in agreement with experiment.

$$\begin{aligned}
A_E = T & \left[1 + \left(\frac{3H\epsilon}{\pi^2 k^2 n_d c T} \right)^2 \kappa_{0d}^2 \right] \left[\left(\frac{\sigma_{0s}}{n_s} (\sigma_{0s} + \sigma_{0d}) + \left(\frac{H}{\epsilon c} \right)^2 \frac{n_s - n_d}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right) \left(\frac{3\kappa_{0s} \mathfrak{S}_s}{\pi^2 k^2 c T} + n_s B_{EN,s}^2 \right) \right. \\
& + \left. \frac{\sigma_{0s} \sigma_{0d}}{n_s \epsilon^2 c} \left(\frac{\sigma_{0s}}{n_s} + \frac{\sigma_{0d}}{n_d} \right) \left(n_s \mathfrak{S}_s - \frac{3\epsilon^2 H^2 \kappa_{0s} B_{EN,s}^2}{\pi^2 k^2 c T} \right) \right] \\
& \times \left[(\sigma_{0s} + \sigma_{0d})^2 + \left(\frac{H}{\epsilon c} \right)^2 \frac{(n_s - n_d)^2}{n_s^2 n_d^2} \sigma_{0s}^2 \sigma_{0d}^2 \right]^{-1} \left[\kappa_{0s} + \kappa_{0d} + \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right)^2 \left(\frac{\kappa_{0s}}{n_s^2} + \frac{\kappa_{0d}}{n_d^2} \right) \kappa_{0s} \kappa_{0d} \right]^{-1} \\
& + \text{a similar term with } s \text{ and } d \text{ interchanged and the sign of } \mathfrak{S} \text{ changed.} \quad (57)
\end{aligned}$$

6.2. Equation (54) is the generalization of the corresponding expression involving the times of relaxation which is only valid at high temperatures, and which has been used by Jones (1936) to discuss the Hall effect in bismuth.* The two cases $n_s = n_d$ and $n_s \neq n_d$ will be considered separately.

Case (i). $n_s = n_d = \frac{1}{2}n$

In this case equation (54) reduces to

$$A_H = -\frac{2}{n\epsilon c} \frac{\sigma_{0s} - \sigma_{0d}}{\sigma_{0s} + \sigma_{0d}}, \quad (58)$$

and A_H is therefore independent of H for all values of H .

Case (ii). $n_s \neq n_d$

Writing, for simplicity, $\sigma_{0s} = \sigma_{0d} = \frac{1}{2}\sigma_0$, (54) becomes

$$A_H = \frac{1}{4\epsilon c} \frac{n_s - n_d}{n_s n_d} \frac{1 - \frac{1}{4} \left(\frac{H}{\epsilon c} \right)^2 \frac{\sigma_0^2}{n_s n_d}}{1 + \frac{1}{16} \left(\frac{H}{\epsilon c} \right)^2 \frac{(n_s - n_d)^2}{n_s^2 n_d^2} \sigma_0^2}. \quad (59)$$

This equation shows that, as H increases, the absolute value of A_H decreases at first (the change being initially proportional to H^2), and reaches the value zero when $H = 2(n_s n_d)^{1/2} \epsilon c \rho_0$. As H increases further, A_H changes sign and increases steadily in absolute value, and for very large fields it approaches the limiting value

$$(A_H)_{H \rightarrow \infty} = -\frac{1}{\epsilon c (n_s - n_d)}, \quad (60)$$

which is independent of the electrical conductivity.

The most extensive experimental work on the field dependence of A_H has been carried out on bismuth and its alloys, which show very marked effects even at room temperature, and which can be discussed by the formal theory (for anisotropic metals) already given by Jones. The sign reversal predicted by equation (59) has been observed in bismuth-lead alloys for a certain range of compositions (Thomas & Evans 1933; see also Jones 1936, p. 663).

The data for the normal metals, which are very scant and unsatisfactory, are discussed in § 7.3.

* Jones's formula is more general than ours in that it applies to anisotropic metals; as was pointed out in § 1.2, however, this is a purely formal generalization of the theory.

6.3. For the Righi-Leduc effect there are again two cases to consider, according as n_s is or is not equal to n_d .

Case (i). $n_s = n_d = \frac{1}{2}n$

$$\text{In this case} \quad B_{RL} = -\frac{6\epsilon}{\pi^2 k^2 n c T} \frac{\kappa_{0s} - \kappa_{0d}}{1 + 4 \left(\frac{3H\epsilon}{\pi^2 k^2 n c T} \right)^2 \kappa_{0s} \kappa_{0d}}, \quad (61)$$

which shows that the absolute value of B_{RL} decreases steadily as H increases. There is no saturation in strong fields, B_{RL} being proportional to H^{-2} for large values of H .

Case (ii). $n_s \neq n_d$

Writing, for simplicity, $\kappa_{0s} = \kappa_{0d} = \frac{1}{2}\kappa_0$, it is found that

$$B_{RL} = \frac{3\epsilon\kappa_0}{4\pi^2 k^2 c T} \frac{n_s - n_d}{n_s n_d} \frac{1 - \frac{1}{4} \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right)^2 \frac{\kappa_0^2}{n_s n_d}}{1 + \frac{1}{8} \left(\frac{3H\epsilon}{\pi^2 k^2 c T} \right)^2 \left(\frac{1}{n_s^2} + \frac{1}{n_d^2} \right) \kappa_0^2}. \quad (62)$$

The behaviour is therefore similar to that of A_H . As H increases, B_{RL} decreases at first in absolute value, changes sign when $H = 2\pi^2(n_s n_d)^{\frac{1}{2}} k^2 c T / (3\epsilon\kappa_0)$, then increases in absolute value and eventually tends to the limiting value

$$(B_{RL})_{H \rightarrow \infty} = -\frac{3\epsilon\kappa_0}{2\pi^2 k^2 c T} \frac{n_s - n_d}{n_s^2 + n_d^2}. \quad (63)$$

6.4. Since there are no experimental results on the field variation of B_{EN}^t and A_E and since the formulae are very complicated, it is not worth while giving such a detailed discussion as for A_H and B_{RL} . The following results give some idea as to the possible behaviour of the coefficients. Considering first B_{EN}^t , neglect the H -variation of $B_{EN,s}^q$, $B_{EN,d}^q$, $\mathfrak{S}_s$ and $\mathfrak{S}_d$, and, as in § 5.3, put $\sigma_{0s} = \sigma_{0d} = \frac{1}{2}\sigma_0$, $\kappa_{0s} = \kappa_{0d} = \frac{1}{2}\kappa_0$,

$$n_s B_{EN,s}^q = n_d B_{EN,d}^q = -3\kappa_0 / (4c\zeta) \quad \text{and} \quad \mathfrak{S}_s = -\mathfrak{S}_d = x\pi^2 k^2 T / \zeta,$$

where $\frac{1}{3} \leq x \leq 1$.

Case (i). $n_s = n_d = \frac{1}{2}n$

Writing $L_n = \frac{1}{3}(\pi k / \epsilon)^2$, $L_0 = \kappa_0 / \sigma_0 T$, $\rho_0 = 1 / \sigma_0$, equation (56) reduces to

$$B_{EN}^t = \frac{3\kappa_0}{nc\zeta} \frac{x \frac{L_n}{L_0} + x - \frac{1}{2} + \frac{1}{2} \left(\frac{H}{n\epsilon c \rho_0} \right)^2 \frac{L_0}{L_n}}{1 + \left(\frac{H}{n\epsilon c \rho_0} \right)^2 \frac{L_0^2}{L_n^2}}. \quad (64)$$

For large values of H this reduces to

$$(B_{EN}^t)_{H \rightarrow \infty} = \frac{3\kappa_0}{2nc\zeta} \frac{L_n}{L_0}. \quad (65)$$

It is readily shown that $\partial B_{EN}^t / \partial H \geq 0$ according as $x \leq \frac{1}{2}$. Hence, at high temperatures, as H increases from zero to infinity, B_{EN}^t decreases steadily from the value (51) to the value (65); at sufficiently low temperatures, however, B_{EN}^t increases as H increases.

Case (ii). $n_s \neq n_d$

In this case the behaviour of B_{EN}^i is complex, but for large values of H

$$B_{EN}^i = \frac{2\pi^4 k^4 c T^2}{3e^2 \zeta \kappa_0 H^2} (n_s + n_d) \left\{ x - \frac{1}{2} + \frac{n_s n_d}{(n_s - n_d)^2} \frac{L_0}{L_n} \right\}, \quad (66)$$

there being no saturation.

6.5. To discuss A_E , the same approximations as in § 6.4 are sufficient.

Case (i). $n_s = n_d = \frac{1}{2}n$

Equation (57) reduces to

$$A_E = \frac{3T}{nc\zeta} \left\{ x \frac{L_n}{L_0} + x - \frac{1}{2} + \frac{1}{2} \left(\frac{H}{nec\rho_0} \right)^2 \frac{L_0}{L_n} \right\}, \quad (67)$$

so that A_E increases steadily with H , the increase being proportional to H^2 for all values of H .

Case (ii). $n_s \neq n_d$

In this case A_E saturates for large H , the saturation value being

$$(A_E)_{H \rightarrow \infty} = \frac{3T}{c\zeta} \frac{n_s + n_d}{n_s^2 + n_d^2} \left\{ x - \frac{1}{2} + \frac{n_s n_d}{(n_s - n_d)^2} \frac{L_0}{L_n} \right\}. \quad (68)$$

It is not at present possible to compare the theoretical results of §§ 6.3 to 6.5 with observation, owing to the lack of sufficient experimental data. Experiments at low temperatures on metals whose electrical resistance does and does not saturate in strong fields are desirable to determine to what extent the behaviour of real metals is in agreement with the predictions of the two-band model.

7. SURVEY OF THE EXPERIMENTAL RESULTS

7.1. It has already been pointed out in § 4.3 that the only reliable measurements on the change of the thermoelectric power are for beryllium. These show that the effect predicted by the single-band model is much too small, but that the results given by the two-band model are correct as regards order of magnitude.

The data on the transverse effects have been referred to in passing in the preceding sections. In the present section the results available are collected together in order to see what conclusions can be drawn from them. The data have been obtained (unless otherwise mentioned) from the survey articles by Borelius (1935) and Meissner (1935), where references to the original experimental papers will be found. Ferromagnetic metals have been excluded from the discussion.

7.2. *The relations among the coefficients.* As was remarked in § 5.3, the relation (35) is a consequence of pure thermodynamics and should therefore be of general validity. Table 1 contains values of the ratio $A_E/A_{EN}T$ derived from the two sources mentioned above. All the values shown refer to ordinary temperatures; there are

as yet no data at all for low temperatures. According to (35), the quantity shown in table 1 should have the value unity for all metals. It is evident from the discrepancies between the two values obtained for one and the same metal that, while there is order-of-magnitude agreement with the theoretical value, the experimental accuracy is quite insufficient to allow any quantitative conclusions to be drawn regarding the extent and significance of the deviations from (35). (The discrepancies are probably to some extent due to the fact that, since the directly measured Ettingshausen-Nernst coefficient is B_{EN} and not A_{EN} , a knowledge of the thermal conductivity κ is required for compiling table 1, and κ has not, in general, been measured on the same specimen as was used for measuring the transverse effects.) Thus a detailed experimental confirmation of (35) will have to wait until the experimental accuracy has been improved (and the measurements have been extended to cover the whole temperature range).

TABLE 1. *Values of $A_E/A_{EN}T$ (to verify equation (35))*

metal	$A_E/A_{EN}T$ from		metal	$A_E/A_{EN}T$ from	
	Borelius, p. 431	Meissner, p. 383		Borelius, p. 431	Meissner, p. 383
Cu	1.05	0.76	Pd	1.23	0.82
Ag	1.22	1.34	Al	1.43	1.73
Au	0.67	0.67	Bi	0.94	2.88
Zn	1.37	4.25	As	0.98	—
Cd	0.75	7.6	Sb	1.25	0.66

TABLE 2. *Values of $B_{RL}/A_H\sigma_0$ and L_0/L_n (to verify equation (45))*

metal	$B_{RL}/A_H\sigma_0$ from		L_0/L_n from	
	Borelius, p. 431	Meissner, p. 383	Borelius, p. 379	Meissner, p. 189
Cu	0.78	0.65	0.92	0.93
Ag	0.87	0.46	0.95	0.97
Au	1.03	0.89	0.96	0.96
Zn	0.85	0.70	0.95	1.02
Cd	0.74	1.24	0.99	0.98
Ir	0.69	—	1.02	1.02
Pd	0.59	0.62	1.06	1.06
Pt	1.9	—	1.03	1.03
Al	0.69	0.49	—	0.89
Bi	2.4	0.035(?)	1.35	1.1 to 1.9
As	—	0.26	—	—
Sb	0.39	0.36	—	1.1 to 1.6
W	—	0.69	1.25	1.18
Mo	—	0.74	1.07	—

Table 2 shows some values of the ratios $B_{RL}/A_H\sigma_0$ and L_0/L_n for room temperature. These ratios should be equal according to equation (45), while at sufficiently high temperatures (45) should reduce to the old relation (34). The discrepancies

between the two values of $B_{RL}/A_H\sigma_0$ obtained for any one metal are to be contrasted with the good agreement in the case of L_0/L_n and show clearly that the experimental data on the transverse effects must be treated with grave suspicion. The experimental accuracy is obviously insufficient to distinguish between (34) and (45) at room temperature or to verify or reject either; and to detect any difference between (34) and (45) one would have to go to temperatures where L_0/L_n is very different from unity. It must be remembered, however, that (45) is no longer valid for the two-band model at low temperatures, so that quantitative agreement may be expected, at best, for the monovalent metals only.

Equation (36), which requires the ratio $A_H A_{EN}/(A_E A_{RL} L_n)$ to be unity, is valid at all temperatures for free electrons, but only at high temperatures for the two-band model. The experimental data for room temperature are shown in table 3, and it is again clear that only order-of-magnitude verification is possible.

TABLE 3. Values of $A_H A_{EN}/(A_E A_{RL} L_n)$ (to verify equation (36))

metal	$A_H A_{EN}/(A_E A_{RL} L_n)$ from		metal	$A_H A_{EN}/(A_E A_{RL} L_n)$ from	
	Borelius, p. 431	Meissner, p. 383		Borelius, p. 431	Meissner, p. 383
Cu	1.09	1.86	Pd	1.56	1.17
Ag	0.84	1.56	Al	0.98	0.90
Au	1.45	1.52	Bi	—	1.15
Zn	0.78	3.2	As	—	5.7
Cd	1.69	1.06	Sb	—	4.1

The present position as regards the relations among the coefficients may be summed up as follows. The old relations (34) to (36) had previously been derived only for free electrons in the limit of high temperatures. The present theory extends the treatment in two ways, first by using a more general model and secondly by considering the whole temperature range. At ordinary temperatures the old relations are found to be effectively unaltered, and the value of the present treatment lies in increasing our confidence in their general validity for real metals. New results are obtained for low temperatures, equation (34) being replaced by (45) for free electrons, and both (34) and (36) being replaced by more complicated expressions for a metal with two overlapping bands; even at low temperatures, however, the new results do not differ from the old ones as regards orders of magnitude. The experimental data available at present all refer to high temperatures and are not sufficiently reliable to be compared in detail with the theory, but there is order-of-magnitude agreement for all metals. To verify the low temperature predictions experiments of greatly improved accuracy are necessary, care being taken that all the effects are measured on the same specimen.

7.3. *The Hall effect in normal metals.* There are few reliable measurements of the Hall coefficients of normal metals at low temperatures or in strong fields. Table 4

contains some values of A_H for various pure metals at different temperatures (but in constant magnetic field). As regards the field variation, the values shown in table 4 are found to be fairly accurately independent of H , even at low temperatures, for fields up to about 10,000 gauss (cadmium is exceptional in showing a somewhat complicated dependence on H which may be due to experimental error).

TABLE 4. *Hall effect in normal metals at different temperatures*

metal	$-A_H \times 10^{15}$ (gaussian units) from Meissner, pp. 338-340		
	290° K	20.3° K	14.5° K
Cu	5.5	7.3	7.3
Ag	8.9	11.3	11.1
Au	8.1	10.9	10.9
Pd	7.6	15.4	15.5
Cd	-6.1	-22.4	-24.8

With the possible exception of cadmium, the temperature variation shown in table 4 and the absence of any field variation could be explained by using the expression (58) for the Hall coefficient of the two-band model and assuming that the relative proportions of the electric current carried by the two bands may vary with the temperature (compare the discussion in § 5.3). For palladium, for example, which is a transition element and which is known from magnetic evidence to have 0.5 electrons per atom in the s -band and the same number of vacant levels in the d -band (Wilson 1939, p. 76), the value of p (the proportion of the total current which is carried by the s -band) required to account for the observations is 0.69 at room temperature and 0.88 at very low temperatures; such values are by no means unreasonable. For the monovalent metals, however, to which the two-band model is least applicable and where the temperature variation of A_H is in any case not very pronounced, it is better to use equation (37) of the free electron model (which requires A_H to be always independent of T and H) as an approximation formula, and to ascribe the observed temperature dependence to some as yet unknown mechanism. The results for cadmium (if genuine) also seem difficult to fit in with the predictions of the two-band model.

There is an almost complete lack of reliable data for liquid helium temperatures, but one interesting result refers to tin, whose Hall coefficient is very small and negative at ordinary temperatures but becomes positive at extremely low temperatures. This behaviour is readily interpreted by means of equation (58) if it is supposed that p is just greater than $\frac{1}{2}$ at high temperatures but just less than $\frac{1}{2}$ at low temperatures.

In general it may be said that the present theory gives, in most cases, qualitatively correct results for the behaviour of A_H over the whole range of temperatures and magnetic fields, and gives detailed agreement in some special cases. However, no complete survey will be possible until much additional experimental evidence has become available, particularly for low temperatures.

7.4. *The temperature variation of the transverse effects.* The remaining coefficients have been measured at ordinary temperatures only. Table 5 contains the results of measurements by Hall (1925, 1937) on all four effects (the same table has been given by Meixner (1939)). At temperatures above the Debye temperature all the quantities shown in table 5 should be independent of T . This follows from our discussion of the one- and two-band models in § 5, but a general proof for the anisotropic case has been given by Meixner (1939), and the result may hence be expected to be a general one for all metals. The table shows that the observed temperature dependence agrees with the theoretical predictions within the probable limits of experimental error, both for the monovalent metals Au and Cu and for the transition element Pd (a curious exception, however, is A_E/T for Au).

TABLE 5. *The temperature variation of the transverse effects at high temperatures*

metal	temperature (°K)	Gaussian units			
		$10^{15}A_H$	10^8TB_{RL}	$10^{15}B_{EN}$	$10^{18}A_E/T$
Au, $\Theta \simeq 175$	345	-7.73	—	—	- 0.39
	330	—	- 8.68	- 6.03	—
	298	—	- 8.94	- 6.03	—
	290	-7.83	—	—	- 1.38
Cu, $\Theta \simeq 315$	358	-5.98	- 1.29	- 6.7	- 1.60
	328	-5.97	- 1.32	- 7.0	- 1.57
	298	-5.96	- 1.45	- 7.2	- 1.60
Pd, $\Theta \simeq 270$	340	—	- 1.29	+ 11.2	—
	337	-9.38	—	—	+ 20.3
	318	-9.50	- 1.33	+ 10.9	+ 18.7
	299	-9.39	—	—	+ 18.0
	298	—	- 1.45	+ 10.9	—

While, at ordinary temperatures, the present theory merely serves to confirm Meixner's general predictions for two special cases, it provides the first theoretical results for the low temperature region. These have been discussed in § 5; they show that the temperature variation is, in general, more complicated than at high temperatures and that there are characteristic differences in the behaviour of the one- and two-band models, especially as regards B_{EN} and A_E . (It must be remembered, however, that no model has yet been worked out for which B_{EN} and A_E are negative at high temperatures, and it is hence dangerous to place too much reliance on the temperature variation predicted by our formulae when considering, e.g., the noble metals). An extension of Hall's measurements to temperatures well below the Debye temperature (and to other mono- and multivalent metals) may be expected to lead to interesting results, but further discussion must be postponed until such measurements have become available.

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Measurements in the reaction zone of a Bunsen flame

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[PLATE 13]

It is possible to make direct measurements in the reaction zone of a Bunsen flame by using a 'low-pressure flame', because the flame is then drawn out and enlarged. The temperature-course through the flame front is measured. The position of the Schlieren picture is deduced and may be compared with the actual photographed Schlieren picture. The heat flow in the reaction zone is calculated; it is found responsible for the formation of a considerable preheating zone.

1. INTRODUCTION

The behaviour of an ordinary Bunsen flame burning with acetylene and oxygen or air at low pressure was described in a former publication (Wolfhard 1943). It was shown that it is possible to burn a mixture of acetylene-oxygen or of acetylene-air down to a few mm. Hg pressure, using a burner of large diameter in a closed

vessel. The diameter of the burner must be increased proportionately (figure 1) in order to obtain a stable flame as the pressure (P) is lowered. The linear extension (b) of the flame is approximately $b \sim 1/P$ in comparable regions of stability, as is seen in figure 1. The regions of stability come together at a certain minimum gas flow which depends on the pressure. In the lowest part of the stability region, the

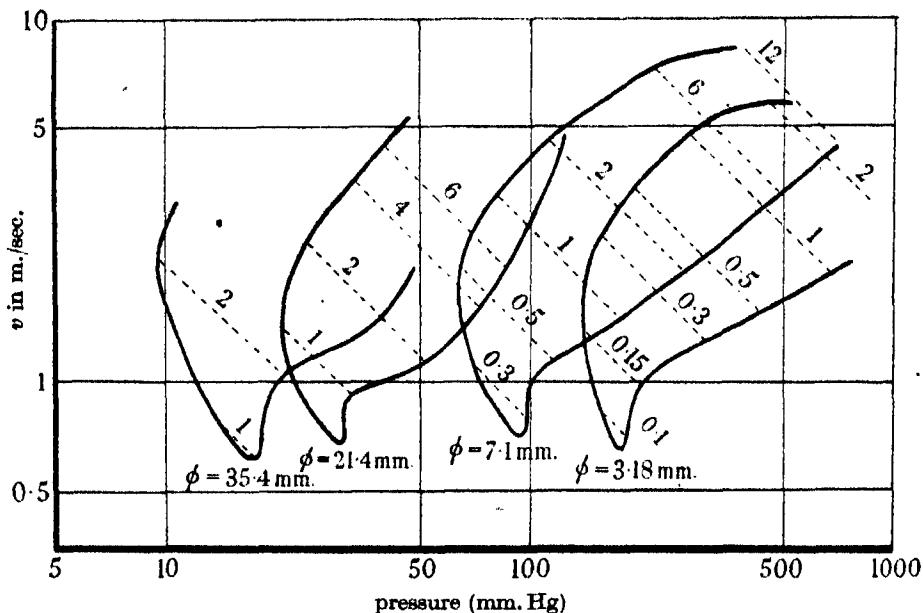


FIGURE 1. Stability regions of the C_2H_2 -air flame for stoichiometric mixture. Ordinate: velocity of the cold mixture in the burner pipe. The numbers in the stability region are the mass-flow of C_2H_2 . ϕ is the diameter of the burner pipe.

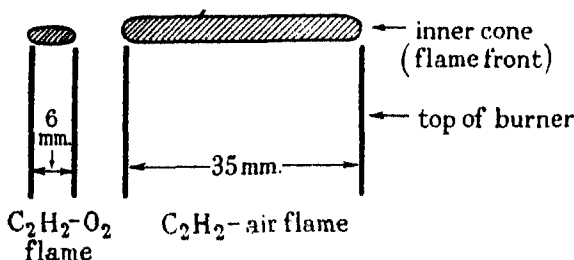


FIGURE 2. The shape of a flame near the 'minimum point': pressure 20 mm. Hg.

flame has an unusual appearance and consists of the reaction zone with the hot gases above it. The outer cone does not exist because the flame is separated. The inner cone lies like a flat disk on the top of the burner (figure 2). It is a very difficult problem to make optical measurements in the reacting zone as long as the inner cone remains cone-shaped. If, however, the reaction zone is effectively a flat disk, then the problem becomes very simple because different parts of the reaction

zone do not overlap. The reaction zone which has at 1 atm. a thickness of about $\frac{3}{100}$ mm. grows bigger when the pressure diminishes. The thickness d is also nearly proportional to $1/P$, so that at 2 mm. Hg we have $d \approx 1$ cm. (the thickness depends also on the composition of the mixture). Such a thick and flat reaction zone is very favourable for the study of its physical and chemical properties.

The reaction zone is visibly not homogeneous. With a stoichiometric mixture it gives, starting from below, a weak green light corresponding to the C_2 -bands; in the middle of the zone the radiation consists essentially of the strong C_2 and CH bands, giving a nearly white light; at the top end of the zone the C_2 -bands disappear and the CH bands are dominant, giving a blue corona (figure 3). The thickness for an acetylene-air flame is somewhat greater than that for an acetylene-oxygen flame, and the diameter of the burner on which the flame must burn is also bigger, hence, at a given pressure, the acetylene-air flame gives a thicker optical layer.

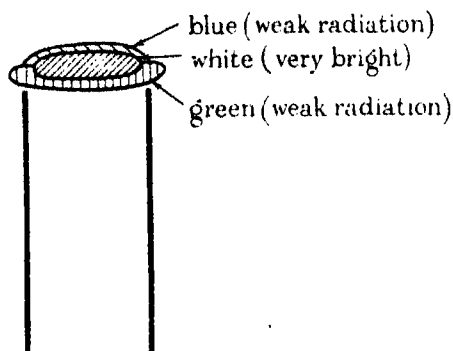


FIGURE 3. The zones of a $C_2H_2-O_2$ flame near the 'minimum point'.

2. THE POSITION OF THE SCHLIEREN PICTURE

Van der Poll & Westerdijk (1941) published a Schlieren photograph of a propane-air flame burning at 1 atm., which showed that the Schlieren picture and the picture of the 'luminous cone' are not the same: it lies distinctly inside the luminous cone. This result was unexpected and important. The Schlieren image must be situated where the gradient of the refractive index (n) is greatest. The refractive index is changed in the reaction zone by the rise in temperature as well as by the change of the components. The temperature rises from about 300 to about 3000° K for an acetylene-oxygen flame. The density after the reaction is therefore $\frac{1}{10}$ of the previous density. The refractive indices of different gases such as C_2H_2 , O_2 , CO, CO_2 , H_2O , vary from $(n-1) \cdot 10^6 = 257$ to 600 at 1 atm. and 0° C. It can only be decided by experiment whether the change of composition or temperature is having the predominant effect in the different parts of the reaction zone. In any case, something important is happening in front of the inner cone before the molecules begin to radiate.

It was necessary first to confirm that this result was not only a property of the propane-air flame, and it was shown that the interesting acetylene low pressure flames already described behaved similarly. At low pressure the absolute change of $(n - 1)$ in the reaction zone is very small, therefore a very sensitive arrangement was necessary (figure 4). The distance from the slit to the Schlieren blind was about 10 m. The whole light beam was shielded by a paper tube to avoid movements of the air. Observation was easy for acetylene-air flames and propane-air flames, but the light emitted from the acetylene-oxygen flame at 1 atm. was so strong, that the Schlieren light, even from a big mercury high-pressure lamp, was scarcely visible. Therefore, for the acetylene-oxygen flame, Schlieren photographs were taken only with an excess of oxygen, so that radiation was reduced. Another difficulty was that the biggest burner for a laminar burning acetylene-oxygen flame at 1 atm. had about 1 mm. diameter, so that the picture of the cone became very small. The two images were usually photographed together, the Schlieren blind being arranged to be drawn from above.

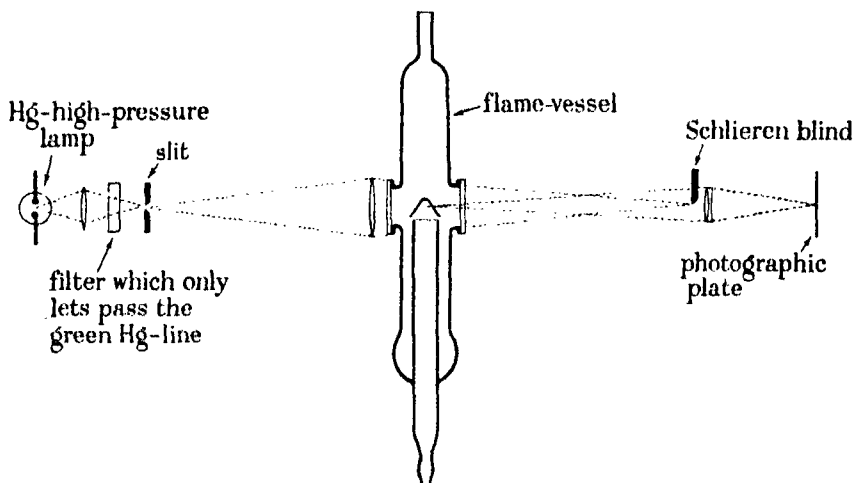


FIGURE 4. Arrangement for the photograph of the Schlieren picture.

Description of the results

(1) Acetylene-air flame

(a) At 1 atm.: The Schlieren image always lies far ahead of the luminous cone, even with excess of oxygen or acetylene: in figure 5, plate 13, the inner cone is the Schlieren image. The distance from the intensity maximum of the Schlieren image from that of the luminous cone becomes a little smaller when the amount of acetylene is decreased.

(b) At low pressure: Below 40 mm. Hg the density, and therefore the absolute change of $(n - 1)$, is too small for a Schlieren image to be obtained without extreme sensitivity. Figure 6, plate 13, shows an inner cone at about 80 mm. Hg. For a flat cone at 40 mm. Hg the Schlieren image lies about 7 mm. in front of the luminous cone.

(2) *Propane-air flame*

Propane-air flames always show a big separation between the two images.

(3) *Acetylene-oxygen flame*

(a) At 1 atm.: The above-mentioned difficulties prevented photographic work, so that only visual observation was possible. With excess oxygen, the Schlieren image was inside the cone; the separation was, however, essentially smaller than for an air flame.

(b) At low pressure: It was not possible to photograph both cones together, because they partially overlap, although the Schlieren image lies somewhat below. It is easy to explain why the separation between the two images is only observable with difficulty for an oxygen flame in comparison with an air flame. The rise of temperature in the reaction diminishes the refractive index. This is, however, counterbalanced by the increase of the refractive index if intermediate organic compounds with higher refractive index are present at the beginning of the reaction. In an air flame, however, the $(n - 1)$ curve is caused almost solely by the temperature, because the amount of N_2 present in the air does not permit so much absolute change of the refractive index by intermediate components which must have a considerable lower concentration. The change of the refractive index by the temperature is however nearly the same as in an oxygen flame, because the ratio of the temperature of the cold mixture and the hot gases is in both cases nearly the same.

The separation of the Schlieren image and the luminous cone is, therefore, a property common to acetylene and propane flames and probably to all hydrocarbon flames, indicating that a rapid rise of the temperature must begin appreciably before the luminosity arises.

In the Schlieren cone the refractive index must become smaller in an upward direction, because the light is refracted downward, as is indicated by the fact that the Schlieren blind must be drawn from above. The temperature effect is therefore predominant.

3. THE TEMPERATURE DISTRIBUTION IN THE REACTION ZONE

The thick and flat nature of the reaction zone of flames burning at a few mm. Hg allows a reasonably accurate measurement of the rise in temperature by means of a thermocouple. It would not be expected that at these low pressures the reaction will take a completely different course because the normal flame velocity is the same in the whole region between 760 and a few mm. Hg for an acetylene-oxygen flame and nearly the same for an acetylene-air flame. The advantages of conducting experiments at low pressure are the following:

(1) At 1 atm. the reaction zone has a thickness of some hundredths of a mm. and therefore a temperature gradient of about 10^5 to 10^6 °C/cm. In such a temperature field, even with very thin wires, there is such a high heat flow that all details are lost. In the low pressure flame the temperature gradient is more than a

hundred times as small, so that there is a possibility of measuring the real increase of the temperature.

(2) At 1 atm. even in an air flame the temperature of the wires becomes so high that a platinum/platinum-iridium thermocouple will melt. Furthermore, platinum wires give a high catalytic effect which will distort the course of the real temperature changes. At low temperature, the heat transfer from gas to wire is smaller, so that the temperature difference between the gas and the wire increases. In an acetylene-oxygen flame at about 5 mm. Hg the temperature of the thermocouple does not rise higher than about 1300° C, so that Hoskins thermocouples (Cromel-Alumel) or Ni-NiCr can be used, the real temperature being estimated afterwards.

(3) The presence of the thermocouple in the flame influences its shape. If the temperature rise is to be measured, the junction of the thermocouple must be visible with a telescope in the image of the luminous flame. In an ordinary flame the surroundings at the tip of the thermocouple are changed in the manner shown in figure 7, hence it is very difficult to measure the position of the thermocouple relative to the flame front. However, if the flame is near the minimum point of the stability region, it has the smallest extension possible at this pressure. Each part of the reaction zone influences the other; if this were not the case, then the flame might be supposed to consist of two independent parts and only one such part would be the smallest flame. The effect of this is that the thermocouple indeed influences the flame front, but only in such a way that the whole flame front rises a little when it is introduced, and the effect is easily corrected.

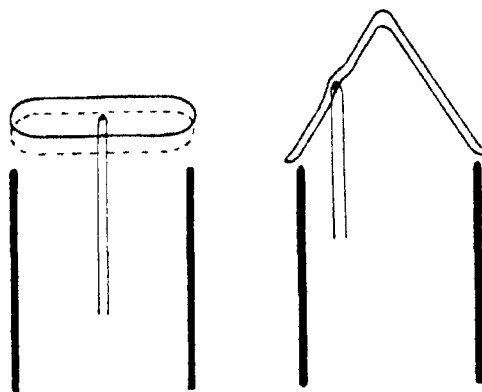


FIGURE 7. The influence of the thermocouple on the flame in different parts of the stability region.

For the measurement of the temperature, the procedure was as follows (figure 8): the thermocouple was brought into the flame from below, supported by tubes of ceramic, which were put one into the other like a telescope. The flow of the mixture of the gases was therefore interfered with as little as possible. The Reynolds number referred to the diameter of the wire was about $\frac{1}{10}$. The thermocouple consisted of

$\frac{1}{10}$ mm. Ni-NiCr or $\frac{3}{10}$ mm. Hoskins: both were used to eliminate the influence of the heat conductivity in the wire. There was a small difference between the measurements, but sufficiently small that the $\frac{1}{10}$ mm. wire could be taken to give nearly the correct temperature distribution across the flame, disregarding the influence

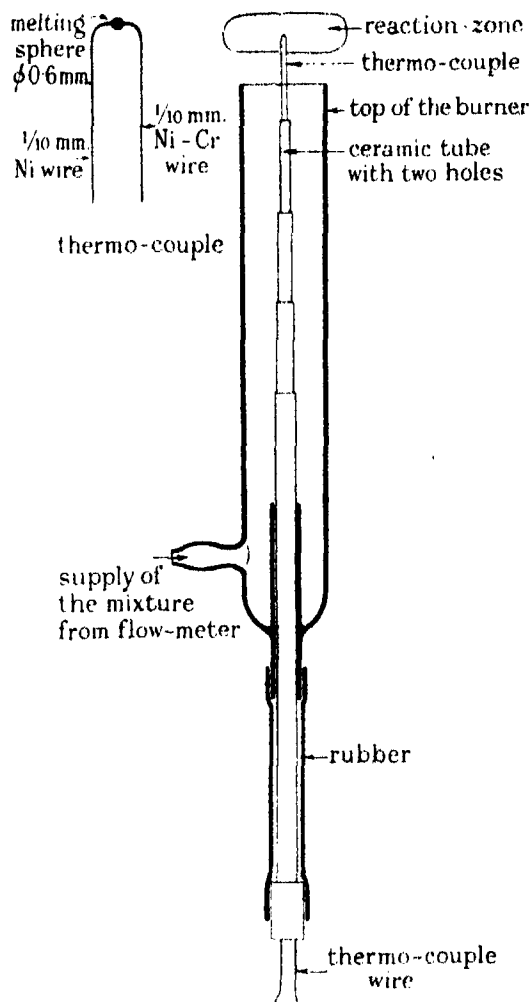


FIGURE 8. Arrangement of the thermocouple.

of radiation. The influence of radiation cannot be eliminated by reducing the diameter of the wire, because both the radiation and the heat transfer from the flame to the wire is a surface effect in contrast to the heat conductivity in the wire which is a volume effect. The thermocouple could be moved up and down so that it was possible to make measurements across the flame front. The thermoelectric e.m.f. was measured with a millivoltmeter whose total resistance was about 5000Ω , and the loss of e.m.f. by the resistance of the thermocouple could be neglected.

The results are shown in figures 9*a* and *b*. The abscissae shows the vertical extension of the flame in mm.; the ordinate the temperature in degrees centigrade and also in $1/T$ ($T = ^\circ \text{abs. temp.}$), and with the scale at the right-hand side the calculated intensity of the Schlieren image (i.e. the slope of the $1/T$ curve). The extension of the flame is plotted in the figures as it is seen in the telescope. The top of the burner is marked; the two lightly shaded inner limits are the contrast zones of the luminous cone: between these limits the intensity is greatest. The two outer limits show the first and last impression of light which could be seen in the telescope. The supposed intensity distribution of the radiation of the luminous zone is drawn in dotted lines.

Attention had to be paid to catalytic effects. These were demonstrated by a platinum wire brought into the flame from below. As soon as its upper end had become red hot, the whole wire glowed down through the whole mixture. The measurements were commenced some cm. below the flame in the cold mixture. The thermocouple was then always raised about 0.5 mm.: the millivoltage, as well as the position of the end of the thermocouple as seen in the telescope, being observed. The voltmeter readings usually vary rapidly. Sometimes, however, it took nearly 10 sec. before the reading stopped changing, thereby indicating that catalytic effects were falsifying the result. A further check as to the presence of catalytic effects is the following: if the thermocouple is far inside the flame, then the leads glow down to the beginning of the reaction zone. The Ni wire showed more catalytic effect than the Ni-Cr wire, the latter bearing an oxide layer. If the Ni wire showed this glow for a longer distance than the Ni-Cr wire then catalytic effects were present. Only flames with an excess of acetylene showed such catalytic effects.

The correction for the error due to radiation is made in the following manner: the end of the thermocouple is a little fused bead of 0.6 mm. diameter between 0.1 mm. Ni and Ni-Cr wires and is covered with an oxide layer from welding. The heat loss is:

$$L = F\sigma T^4 s$$

$s = \text{emission coefficient,}$
 $F = \text{area of the sphere.}$

The heat transfer to the wire is:

$$Q = \alpha F(T_2 - T_1)$$

$T_2 = \text{temperature of gas,}$
 $T_1 = \text{temperature of thermocouple.}$

The heat transfer coefficient (α) depends on Nusselt's number (Nu):

$$Nu = \frac{\alpha d}{\lambda}$$

$d = \text{diameter of the sphere,}$
 $\lambda = \text{heat conductivity coefficient.}$

The Nu number depends on the Reynolds number, which can be calculated exactly:

$$Re = \frac{vd\rho}{\mu}$$

$v = \text{velocity of the gas in the flame,}$
 $d = \text{diameter of the sphere,}$
 $\rho = \text{density of the gas,}$
 $\mu = \text{viscosity.}$

The dependence of $Nu = f(Re)$ has only been measured for a long straight wire by Hilpert (1933) and King, and also only for Reynolds numbers down to about 1. The dependence of the Nusselt-number on the Reynolds number is assumed to be nearly the same for a straight wire as for a sphere, so that the difference in temperature between the thermocouple and the flame can be estimated. It is not necessary for this correction to be absolutely exact, because in these measurements only the relative vertical distribution of the temperature is of interest.

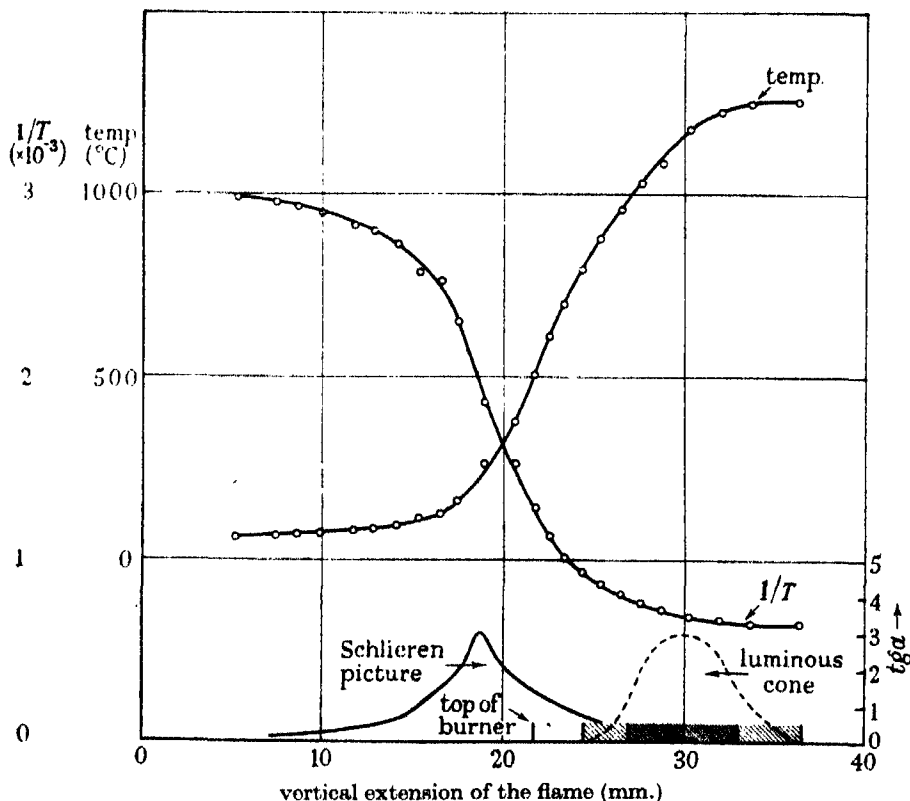


FIGURE 9a. Temperature distribution of a $C_2H_2-O_2$ flame. Pressure 4.3 mm. Hg. $1.90 \text{ cm.}^3/\text{sec. } C_2H_2$. $12.2 \text{ cm.}^3/\text{sec. } O_2$.

Consider now the course of the temperature curve in figure 9b, beginning some cm. below the flame in the cold mixture. The thermocouple shows a temperature perhaps 20°C too high. The whole vessel is heated and therefore also the quartz tube containing the thermocouple. By heat radiation it acquires a somewhat higher temperature than the mixture is supposed to have. At 12.4 cm. the rise of temperature begins. The position in which this first rise takes place is definite and is not affected by external factors. The temperature increases now with a gradient of about $1.5 \times 10^3^\circ \text{C cm.}^{-1}$. By comparison of the temperature gradient obtained

with the 0.3 and 0.1 mm. wire thermocouple the true gradient is estimated to be about 10 % higher than represented in figure 9b. A correction of such a size does not cause much change in the character of the curve. Catalytic effects do not seem to affect this measurement. A short distance beyond the reaction zone the temperature decreases again due to heat loss by radiation and the heat conductivity of the gas. Plotting $1/T$, the gradient of the density, and with it the gradient of the refractive index, is obtained. The maximum of this gradient gives the position of the Schlieren

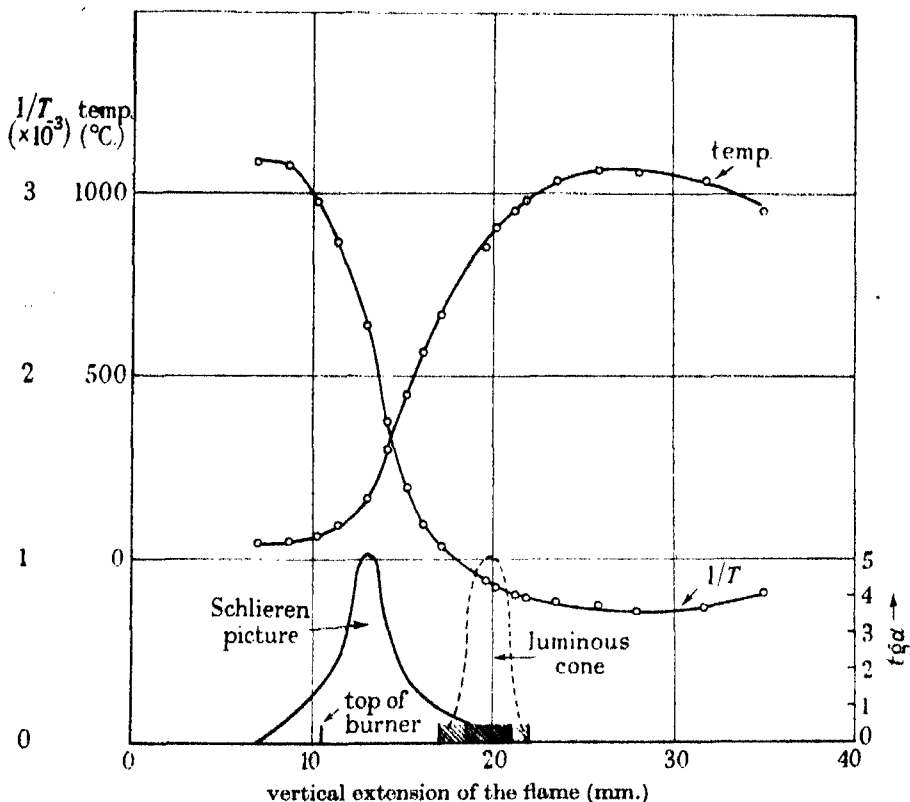


FIGURE 9b. Temperature distribution of a C_2H_2 -air flame. Pressure 14.8 mm. Hg. $1.15 \text{ cm.}^3/\text{sec. } \text{C}_2\text{H}_2$. $16.5 \text{ cm.}^3/\text{sec. air}$.

image. It is seen that the Schlieren image should be far in front of the visible flame front, as is observed in the experiment. Thus it is shown that the temperature rise begins far before the radiation from the C_2 and CH molecules commences. Figure 9a gives a temperature curve of an oxygen-flame at 4.3 mm. Hg. Figure 10 gives the distance of the maximum of the Schlieren image from the intensity maximum of the luminous region, depending on the percentage of the acetylene in air or oxygen. Especially good agreement is shown by the fact that the distance decreases a little with decrease of the acetylene in the mixture. It was not possible to use the same

excess of acetylene with an oxygen flame as for an air flame, so both curves do not cover the same range, but it will be noticed that the distance between the centre of the Schlieren image and the luminous cone is smaller for an oxygen than for an air flame. For this comparison the pressure of the flames was reduced to 10 mm. Hg, making use of the relation that the linear extension of the flame is inversely proportional to the pressure. This fact, together with the possibility of the presence of intermediate organic compounds (see above), explains the difficulties of the separation and the partial overlapping of the two graphs for an oxygen-flame.

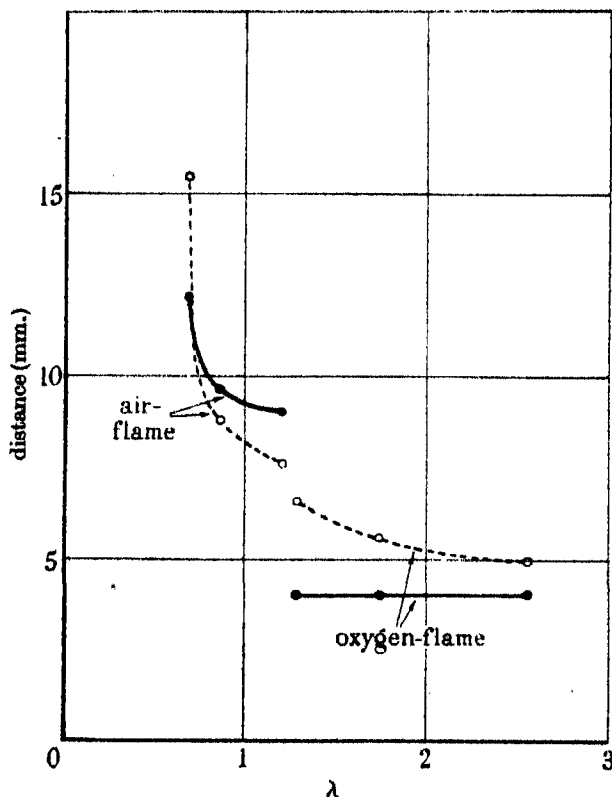


FIGURE 10. Distance between centre of Schlieren and flame-light pictures, and thickness of flame-light cone. ---- complete thickness of flame-light cone, — distance between top of Schlieren picture and flame-light cone. Pressure reduced to 10 mm. Hg. $\lambda = \text{air}/11.9 \times C_2H_2$ for air flame, $\lambda = O_2/2.5 \times C_2H_2$ for oxygen flame.

The determination of the temperature distribution across the acetylene-oxygen flame (figure 9a) is more accurate than that for the acetylene-air flame (figure 9b) because the pressure is lower, and therefore the extension of the flame is longer. Therefore, this curve is worth more detailed consideration.

Errors due to the radiation from the thermocouple must first be corrected, and so the curve t (corr.) obtained (figure 11). The highest temperature may be wrong by about 300°C , but this does not change the character of the curve. In the



FIGURE 5. Schlieren picture of a C_2H_2 -air flame at 1 atm.



FIGURE 6. Schlieren picture of a C_2H_2 -air flame at 80 mm. Hg.

(Facing p. 522)

middle part of the curve (about 2.0 cm.) there is a temperature gradient of $250^{\circ}\text{C}/\text{mm}$. This means that a heat current B streams in the direction of the cold mixture.

$$B = \lambda F \frac{\partial t}{\partial x}$$

λ = heat conductivity coefficient,
 F = area of the flame,
 $\partial t / \partial x$ = temperature gradient.

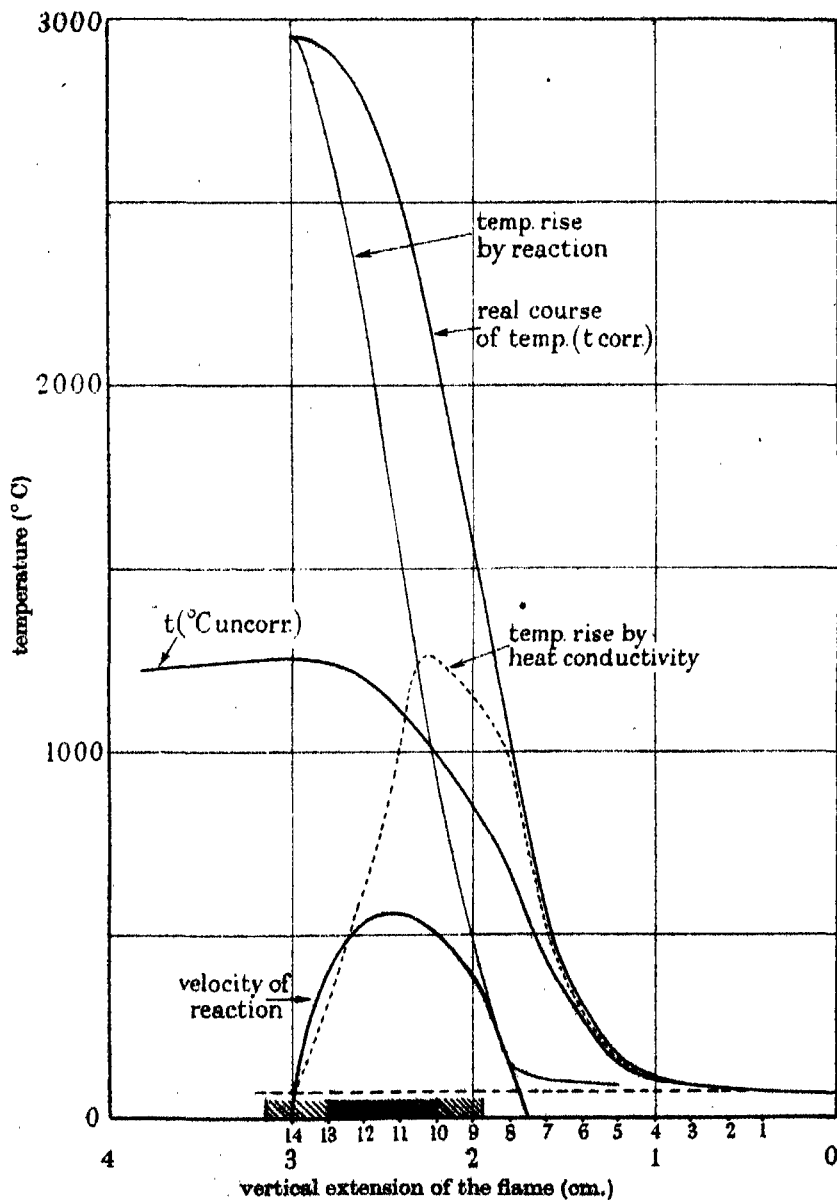


FIGURE 11. The heat conductivity in the flame. $\text{C}_2\text{H}_2\text{-O}_2$ flame. 4.3 mm. Hg.
 1.90 cm.²/sec. C_2H_4 . 12.2 cm.²/sec. O_2 .

Dividing the vertical extension of the flame into different sections, sections (1 to 2); (2 to 3); (3 to 4) ... and considering the section (9 to 10), the slope of the curve is nearly the same at position 9 as at 10, therefore as much heat is coming in at 10 as going out at 9. The rise of the temperature (about 500°C) is therefore caused entirely by the reaction. The change occurs where the slope of the curve is not constant. Considering the section (6 to 7), at 7 there is a heat flow $B = 7.4 \text{ kcal./h}$; at 6 a heat flow of $B = 3.0 \text{ kcal./h}$. The difference of 4.4 increases the temperature by about 270°C . The rise of temperature is the same within the accuracy of the measurement. This means that no reaction is necessary in this region to explain the temperature rise. Such calculations can be made for all sections, and so the result is obtained that up to the centre of the section (7 to 8) the whole rise of the temperature can be explained by the heat flow due to conductivity alone. The dotted curve gives the rise of the temperature due to the change of the slope of the measured temperature curve and, to a smaller extent, to the temperature dependence of the heat conductivity coefficient. Considering next section (12 to 13), in this case more heat is coming out than is going in. This means that the heat flow from that region reduces the temperature rise which would be caused by the reaction alone. The dotted line therefore drops in this part of the flame zone. The difference between the measured temperature curve and the dotted line is the temperature curve which would be caused by the reaction alone. The slope of this curve is the reaction velocity (strong line). The accuracy of the reaction velocity curve obviously cannot be very high, and it is therefore unprofitable to consider any further the reaction velocity curve in relation to the location of the visible flame picture; that must wait until more accurate measurements are available. These could be obtained by conducting experiments at about 1 mm. Hg , or with thinner thermocouples.

The facts which can be gathered from this investigation are:

1. The heat flow heats the cool mixture to a temperature of about 800°C . The usual ignition temperatures lie at about 300°C for acetylene-oxygen and acetylene-air flames, but at 1 atm. with an oxygen flame we have induction times of about $1 \times 10^{-6} \text{ sec.}$ in the flame, and it is very uncertain if a temperature of 800°C is sufficient to explain the start of inflammation as a thermal explosion.

2. The heat flow forms a preheating zone which is larger in an air flame than in an oxygen flame.

3. The Schlieren picture shows in the first temperature rise at about 200°C . In this region the whole temperature rise is due to heat conductivity, and the reaction velocity seems to be zero.

We wish to thank Sir Alfred Egerton for his interest in the work and for his help in its preparation for publication.

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The influence of incombustible vapours on the limits of inflammability of gases and vapours in air

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The influence of some incombustible vapours upon the upward propagation of flame through mixtures of combustible gases and vapours with air contained in a $1\frac{1}{2}$ in. glass tube has been examined and some comparisons made with results in a 4 in. tube. From the data obtained with the smaller tube it has been possible to plot diagrams for each of the combustibles with inert vapour and air showing completely the compositions of inflammable and non-inflammable mixtures. From these, the limiting 'safe' composition of mixtures of inert vapour with air and with the combustible respectively have been derived.

The combinations studied were hydrogen, methane, ethylene, carbon monoxide, *n*-hexane, cyclohexane and benzene with methyl bromide; hydrogen and *n*-hexane with difluorodichloromethane, and methane with carbon tetrachloride. A sample of coal gas, the composition of which was determined, has also been examined with methyl bromide as the inert vapour, and it is shown that the limit curve agrees fairly well with that calculated by Le Chatelier's rule from the curves for its constituents.

INTRODUCTION

It is well known that the limits of inflammability of combustible gases in air are narrowed and ultimately extinguished by additions of incombustible gas or vapour. A large amount of actual data on this subject has been collected by Coward & Jones (1938) and there have been more recent publications on the subject too numerous to mention individually.

Recent tendencies in connexion with fire extinguishing techniques have however aroused interest in certain materials, concerning which the literature provides only limited information. Outstanding among these is methyl bromide. Another material which has practical possibilities as a fire extinguisher at the present time is difluorodichloromethane (freon 12), which has hitherto found its chief use as a refrigerant.

Dufraisse, Vieillefosse & Le Braz (1933) showed that, under specified conditions, 10 % of methyl bromide in the air supply extinguished the flame of coal gas burning at a jet, and Olsen & Graddis (1938) published the results of some measurements relating to the suppression of flame propagation in methane-air mixtures. On plotting their figures in a suitable manner, it is found that they indicate that the presence of 5.3 % of methyl bromide in air suppresses flame propagation with methane in any proportion, and that the presence of 41.2 % in methane suppresses flame propagation in air.

This incomplete information has now been supplemented by systematic measurements from which limits of inflammability have been plotted completely for

ternary systems comprising methyl bromide and air, together with representative combustible gases and vapours. The combustibles concerned are hydrogen, carbon monoxide, methane, ethylene, a sample of coal gas of known composition, and the vapours of *n*-hexane, cyclohexane and benzene.

Measurements have also been made with freon, but referring only to hydrogen and *n*-hexane as the combustibles. However, the systematic measurements with methyl bromide, as well as existing data with carbon dioxide and nitrogen as extinguishers, allow a reasonable estimate of its effect on other combustibles to be made from these two cases along with those of methane (Jones & Perrott 1930), propane and *n*-butane (Jones & Scott 1946).

Finally, the effect of carbon tetrachloride on methane-air flames has been studied. This has already been done by Coward & Jones (1926) and thus a link is provided between our present work and that of the U.S. Bureau of Mines, where, in work extending over many years, experimental conditions similar to our own have been employed.

EXPERIMENTAL

Apparatus and method

General. The conditions adopted for the main determinations of limits of inflammability were similar to those defined by Jones (1929) as being reasonably representative of conditions in large volumes of gas. The tube in which mixtures were prepared and submitted to test for flame propagation was of pyrex, about 5 ft. long and 1½ in. bore. It was set up vertically with the upper end closed and for the purpose of testing the prepared mixture the lower end was momentarily uncovered and a 1 in. coal gas flame applied. If flame then propagated throughout the complete length of the tube the mixture was considered to be within the limiting composition, but not otherwise. In order to verify the assumption that an increase in tube diameter over the figure given does not materially alter the limits, selected mixtures were examined using a 4 in. diameter tube, but otherwise under the conditions described.

Two different methods were employed for preparing the mixtures to be tested. When using the combustible gases (hydrogen, carbon monoxide, methane, ethylene, and coal gas) with methyl bromide a flow method was used. Although this was somewhat extravagant of materials it eliminated mixing difficulties, which, as is well known, can be serious with a long tube. For mixtures incorporating vapours of substances liquid at ordinary temperatures (hexane, cyclohexane, benzene and carbon tetrachloride) the flow method is less simply applied, and a static method was preferred, in which the tube was evacuated, the mixture made up from its constituents by pressures, and thoroughly mixed by means of a fan as used by Egerton & Powling (1948). The two methods are described in detail in the following paragraphs.

Flow method. Into the upper end of the ignition tube were fed continuously the three gases composing the mixture for test (combustible, air and methyl bromide).

These were stored in cylinders and their rates of flow were controlled by reducing valves followed by hand-operated needle valves, using calibrated capillary flow gauges for observation. In the case of methyl bromide the reducing valve was not needed, but in order to avoid cooling of the liquid by evaporation the container was immersed in a large volume of water at room temperature.

The relative rates of flow of the gases determined the composition of the mixture flowing down the ignition tube. Mixing was facilitated by means of a glass wool plug in the head of the tube and there was every indication that this was quite effective. The total rate of flow of mixture was controlled so that the tube was swept out once in about 30 seconds.

The lower end of the ignition tube was closed by a brass disk, carrying a $\frac{3}{4}$ in. lead-off tube for waste gases, and seating on a flange sealed to the ignition tube. In order to test the inflammability of the mixture in the tube at any time, the brass disk was slid off and a 1 in. coal gas flame applied to the mouth of the tube. A critical point was normally decided on ten failures to propagate or two propagations, whichever first occurred. The difference between a pair of points, one within and the other outside the limit of inflammability, did not usually exceed 2 mm. of flow gauge head. This represented from 1 % of the amount of the component of which there was most in the mixture under consideration, to a maximum of 3 % of a component of which there was only a small proportion present.

In order to extinguish flames which continued to burn at the top of the tube following propagation, a fourth gas connexion was provided through which carbon dioxide could be introduced if required.

On account of the low luminosity of hydrogen-air flames, a platinum resistance thermometer in a balanced bridge circuit was installed at the head of the ignition tube for the purpose of detecting such flames. A thermocouple detector was also used with these and other mixtures.

Before the apparatus was developed into the form described, the question of technique was carefully considered, and a number of preliminary tests were carried out. It was shown by means of comparative measurements upon stationary mixtures, that the small downward velocity imparted to the gases had no appreciable effect upon the location of the limits of flame propagation. That this is so is due to the fact that flame speeds do not fall off progressively to zero as the limit is approached, but always have a finite value even at the limit. If, then, the rate of linear flow of the gases is small compared with the limit flame speed, the readings of limit mixture composition are not affected.

In experiments with the lower end of the ignition tube open to the atmosphere it was found that, in spite of the downward gas flow there was evidence of a tendency for air to diffuse a short distance up the tube, thus weakening the prepared mixture.

Static method. The apparatus used for measurements involving vapours of materials liquid at ordinary temperatures is illustrated diagrammatically in figure 1. The pyrex ignition tube, which was of the standard dimensions previously

specified and was closed at the lower end by a vacuum-tight removable brass cap, was evacuated together with the blower and circulating tubes by means of a hyvac pump. The liquid constituent was allowed to evaporate into the circuit from a bulb until the required pressure, as indicated by the mercury manometer, was reached. The other gas or vapour was similarly admitted, as required, from a cylinder controlled by a needle-valve. The blower was started and air was let in through calcium chloride, a length of capillary tube limiting its rate of entry. When atmospheric pressure had been reached and the constituents well mixed the blower

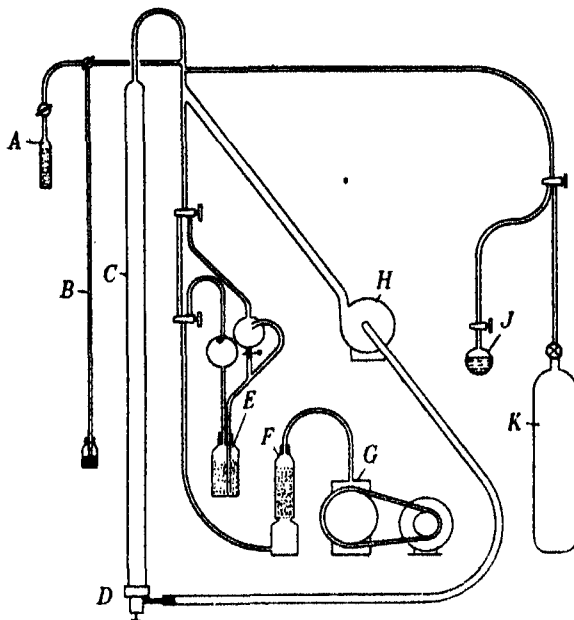


FIGURE 1. Static method. Key to diagram: *A* air inlet via calcium chloride drying tube; *B* mercury manometer; *C* ignition tube; *D* vacuum-tight removable brass cap; *E* scrubber (potassium hydroxide solution) with spray trap and catchpot; *F* potassium hydroxide drying tower; *G* hyvac pump; *H* blower-mixer; *J* bulb containing liquid constituent; *K* gas cylinder.

was stopped, the brass cap removed from the ignition tube and the standard flame applied. After the test air was drawn through the ignition tube by the hyvac pump, sweeping the contents through the caustic potash scrubbers. The cap was then replaced and re-evacuation commenced.

The condensable vapours were, of course, absorbed very rapidly by rubber surfaces and especially by rubber grease. The former were minimized by using butted joints for glass tubes; hydrocarbon-resistant lubricants were used for glass taps. Some difficulty was at first experienced in obtaining a good vacuum seal at the cap without the use of lubricant. The detail diagram in figure 2 shows the method by which this was overcome. A totally enclosed rubber washer was compressed by means of a screw on to a $\frac{3}{8}$ in. flange round a $\frac{3}{8}$ in. hole.

Preliminary determinations were made with a form of apparatus in which the constituents assembled in the ignition tube were stirred by a manually operated piston. This was carried on a wire which left the top of the tube through two coaxial rubber tubes tightened on to it with a screw clip. Glycerol was used as lubricant.

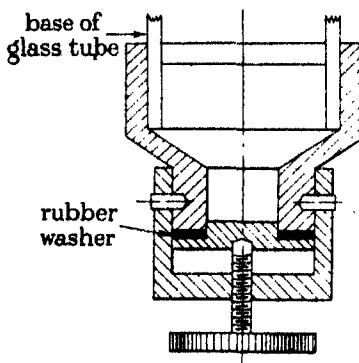


FIGURE 2. Detail of brass closure.

Results obtained with the later form of apparatus showed no marked differences from the preliminary ones, but the improved method of stirring was less laborious and could be operated during admission of air to complete the mixtures. The latter was found to be desirable on account of a tendency for vapours to condense on the tube walls due to regional compression as air was admitted to the stagnant mixture. Such condensate was not easily re-evaporated by piston mixing.

Materials. The sources and characteristics of the materials employed are given below. The gases, with the exception of air in the static method, were not specially dried. Being derived from high-pressure cylinders however, their moisture content should be unimportant for present purposes. In the case of the liquids, benzene, hexane, and cyclohexane, a considerable amount of vapour was pumped off before use. The last part of the liquid was also rejected so that only the middle fraction was employed in the tests.

(1) *Hydrogen.* From the British Oxygen Co. Ltd. Guaranteed purity of 99.2 to 99.5 %. Analysis by combustion showed 99.6 %.

(2) *Carbon monoxide.* Prepared by the reaction of formic and sulphuric acids at 100° C. The product was freed from acid gases by scrubbing with caustic potash solution and compressed. It showed more than 99 % absorption in ammoniacal cuprous chloride.

(3) *Methane.* Derived from colliery blowhole gas (initially 96.5 %) which was freed from CO₂ by caustic potash and liquefied. The liquid was evaporated under pressure into cylinders, giving a product of practically 100 % purity.

(4) *Ethylene.* From the British Oxygen Co. Ltd. Prepared by the reaction of ethyl alcohol with sulphuric acid. Had a guaranteed purity of 97.5 % rising to 99 %, 99.4 % found to be absorbed by fuming sulphuric acid.

(5) *Coal gas*. Compressed from mains supply (Gas Light and Coke Co. Ltd.): benzole extracted. Found by analysis to have the following composition: CO_2 , 2.7 %; unsaturated hydrocarbons, 3.4 %; O_2 , 1.0 %; CO , 12.3 %; H_2 , 48.6 %; CH_4 , 20.6 %; C_2H_6 , 0.6 %; N_2 (by difference), 10.8 %.

(6) *Benzene*. 'Crystallizable'. From Hopkin and Williams Ltd.

(7) *n-Hexane*. B.D.H. Laboratory Reagent ('free from aromatic hydrocarbons').

(8) *Cyclohexane*. From Research Laboratory, Eastman Kodak Co., Rochester, N.Y.

(9) *Air*. Compressed from laboratory atmosphere without special treatment of any kind for the flow method. Drawn from atmosphere through calcium chloride for the static method.

(10) *Methyl bromide*. From May and Baker Ltd. 'Pure' grade.

(11) *Carbon tetrachloride*. From Hopkin and Williams Ltd. 'Pure' grade.

(12) *Freon 12*. From the Frigidaire Corporation. A low temperature vacuum distillation revealed the presence of a small amount of impurity less volatile than freon 12. In practice, therefore, the last 10 to 20 % of the contents of a cylinder were rejected. The fraction used had a vapour density agreeing within the limits of measurement with the formula density of CCl_2F_2 .

Results

Influence of tube diameter on limits for combustible-air mixtures. Comparative measurements were made, in 1½ in. and 4 in. diameter pyrex tubes, of the limits in air of hydrogen, carbon monoxide, ethylene, *n*-hexane and cyclohexane. The results are given in Table 1. As far as lower limits are concerned there is evidently little effect of tube diameter above 2 in.* This is in accordance with accepted data.

Figures for the upper limits call for more consideration. Those for hydrogen and carbon monoxide show little diameter effect, but with hexane and with ethylene there is a rather unexpected lowering with increase of tube diameter.

TABLE 1. INFLUENCE OF TUBE DIAMETER ON LIMITS OF INFLAMMABILITY
IN AIR (STATIC METHOD)

combustible	limits (%) in 1½ in. tube		limits (%) in 4 in. tube	
	lower	upper	lower	upper
hydrogen	4.0	73.8	4.0	75.0
carbon monoxide	15.8	68.5	14.5	68.4
ethylene	3.15	†	3.20	22.7
cyclohexane	1.50	—	1.33	6.20
<i>n</i> -hexane	1.45	7.50	1.45	5.70

† 32.0 using flame detector; 28 to 29% by visual observation.

Use of flame detector. The use of a resistance thermometer or thermocouple as flame detector at the top of the tube was found to facilitate the placing of limits in most cases, but was indispensable for the lower limit of hydrogen on account of

* The discrepancy between the lower limits for carbon monoxide is not more than is to be expected, in this case, in experiments in which the moisture content of the gases is not strictly controlled.

low luminosity. In general, a substantial throw was registered within the inflammable range, no matter how close to the limit. In other words, there was a discontinuity in the magnitude of the throw in passing through the limit. The lower limit of hydrogen provided an exception, however, for here the throw decreased regularly to zero at the limit. No doubt this exceptional behaviour is connected with the fact, first noted by Coward & Brinsley (1914), that as the lower limit for hydrogen (upward propagation) is approached combustion becomes progressively less complete. In the presence of more than about 10 % of methyl bromide the variation of throw at the lower limit of hydrogen became discontinuous.

In only one case did the use of the flame detector reveal anything entirely unexpected. This was with ethylene (static method), with which the detector continued to give throws well above the visually estimated upper limit of 28 to 29 %. With the aid of the detector the upper limit was finally located at 32.0 %. In the 4 in. tube however the detector indicated no flame capable of indefinite propagation above the visual upper limit, which was 22.7 %.

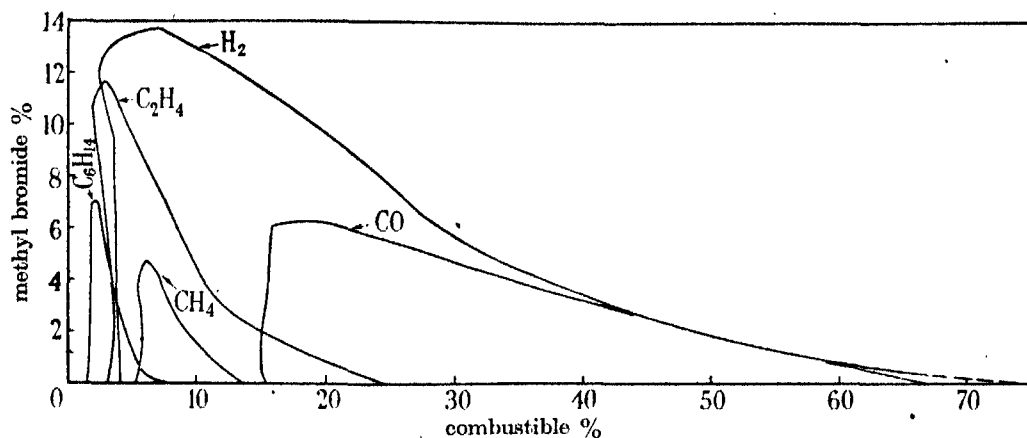


FIGURE 3. Limit curves.

Limits of inflammability of combustible-methyl bromide-air mixtures. In figure 3 the limit curves as determined in a 1½ in. tube for hydrogen, carbon monoxide, methane, ethylene (flow method) and *n*-hexane vapour (static method) with air and methyl bromide are shown together. In these diagrams the limiting percentages (on a basis of volume) of combustible and methyl bromide for flame propagation under the conditions of measurement, are plotted respectively as abscissa and ordinate. The balance to 100 % at any point represents the proportion of air. All points in the areas enclosed by the curves represent mixtures of the three constituents which are capable of flame propagation under the experimental conditions described. Points outside the curves represent mixtures which are incapable of flame propagation.

The upper limit for hydrogen in the absence of methyl bromide was not determined in the flow apparatus but a value of 73.8 % was obtained in the static

apparatus and this has been adopted. The adjacent part of the extinction limit curve was interpolated to meet the part determined experimentally, and is shown by a broken line in figure 3.

The relations given in these diagrams are the result of drawing smooth curves through experimentally determined points representing mixtures on the limit of flame propagation. From large scale drafts of these, points were read off systematically and are tabulated in table 2. The table also contains the results for coal gas, cyclohexane and benzene, and for *n*-hexane in a 4 in. tube. The vapour pressures of cyclohexane and benzene at the laboratory temperatures prevailing when this work was done were insufficient to enable their upper limits (in absence of methyl bromide) to be reached. The fact that the area of inflammability of the hexane-methyl bromide system was found to be less in the 4 in. than in the smaller tube is difficult to explain. It seems however that this observation is associated

TABLE 2. COMPOSITION OF MIXTURES (INCORPORATING METHYL BROMIDE) AT THE LIMIT OF INFLAMMABILITY, DERIVED FROM SMOOTHED CURVES

methyl bromide (%)	hydrogen		carbon monoxide		ethylene	
	lower	upper	lower	upper	lower	upper
0	4.0	73.8*	15.3	67.4	3.0	24.5
0.5	4.0	64.0	15.0	62.5	3.25	21.8
1.0	4.0	57.5	15.0	57.8	3.4	19.25
1.5	3.9	52.5	15.0	53.6	3.55	17.0
2.0	3.9	48.3	15.1	49.6	3.6	15.0
2.5	3.8	45.0	15.2	45.6	3.6	13.35
3.0	3.8	41.8	15.3	41.9	3.5	12.1
3.5	3.8	39.2	15.4	38.3	3.45	11.2
4.0	3.8	36.7	15.5	34.8	3.4	10.45
4.5	3.7	34.5	15.5	31.5	3.3	9.95
5.0	3.7	32.5	15.6	28.2	3.2	9.45
5.5	3.7	30.7	15.6	25.0	3.1	8.95
6.0	3.7	29.0	15.7	21.3	3.0	8.5
6.5	3.6	27.6	—	—	2.9	8.0
7.0	3.6	26.3	—	—	2.8	7.55
7.5	3.6	25.2	—	—	2.7	7.05
8.0	3.6	24.1	—	—	2.55	6.55
8.5	3.5	22.9	—	—	2.45	6.05
9.0	3.5	21.7	—	—	2.3	5.6
9.5	3.5	20.5	—	—	2.1	5.1
10.0	3.2	19.1	—	—	2.0	4.6
10.5	3.0	17.8	—	—	1.95	4.1
11.0	2.7	16.4	—	—	2.0	3.65
11.5	2.5	14.8	—	—	2.35	3.15
12.0	2.4	13.3	—	—	—	—
12.5	2.5	11.6	—	—	—	—
13.0	3.1	9.8	—	—	—	—
13.5	5.3	7.8	—	—	—	—
peak (%):						
combustible		6.7		17.7		2.75
methyl bromide	13.7		6.2		11.65	

TABLE 2 (cont.)

methyl bromide (%)	methane		coal gas		n-hexane	
	lower	upper	lower	upper	lower	upper
0	5.20	13.50	5.0	33.0	1.45	7.50
0.5	5.52	12.14	5.15	27.9	1.50	5.75
1.0	5.70	11.00	5.3	26.4	1.55	5.3
1.5	5.80	10.02	5.4	24.4	1.60	4.9
2.0	5.80	9.20	5.55	23.0	1.65	4.6
2.5	5.72	8.56	5.65	21.85	1.70	4.25
3.0	5.54	8.00	5.8	20.8	1.70	3.95
3.5	5.40	7.54	5.9	19.85	1.75	3.7
4.0	5.46	7.12	6.0	18.95	1.75	3.5
4.5	5.64	6.56	6.1	18.0	1.75	3.3
5.0	—	—	6.1	17.1	1.75	3.1
5.5	—	—	6.0	16.2	1.75	2.9
6.0	—	—	5.8	15.35	1.75	2.7
6.5	—	—	5.65	14.5	1.75	2.5
7.0	—	—	5.45	13.7	1.90	2.25
7.5	—	—	5.2	12.9	—	—
8.0	—	—	5.0	12.1	—	—
8.5	—	—	4.75	11.2	—	—
9.0	—	—	4.5	10.3	—	—
9.5	—	—	4.2	9.25	—	—
10.0	—	—	4.05	8.1	—	—
10.5	—	—	4.15	6.8	—	—

peak (%):

combustible	6.0	4.85	2.1
methyl bromide	4.7	11.0	7.05

methyl bromide (%)	cyclohexane		benzene		n-hexane in 4 in. tube	
	lower	upper	lower	upper	lower	upper
0	1.50	†	1.65	†	1.45	5.70
0.5	1.55	†	1.70	†	1.50	5.1
1.0	1.55	†	1.75	†	1.55	4.65
1.5	1.60	†	1.80	†	1.60	4.3
2.0	1.65	†	1.85	†	1.65	4.0
2.5	1.70	†	1.90	†	1.70	3.8
3.0	1.75	†	1.95	†	1.75	3.6
3.5	1.80	†	2.00	†	1.80	3.45
4.0	1.80	†	2.05	†	1.85	3.3
4.5	1.85	†	2.10	†	1.90	3.15
5.0	1.90	†	2.15	†	1.95	2.95
5.5	1.95	†	2.15	3.35	2.0	2.7
6.0	2.00	3.3	2.15	3.05	—	—
6.5	2.00	3.1	2.05	2.85	—	—
7.0	2.05	2.8	1.90	2.60	—	—
7.5	—	—	1.95	2.45	—	—

peak (%):

combustible	2.25	2.25	2.2
methyl bromide	7.4	7.75	6.0

* Value determined in static apparatus.

† Not determined by the authors.

with that already recorded (see table 1)—that the ordinary upper limit for hexane in air is lowered in the wider tube.

The lowering effect of methyl bromide on the lower limit of some of the combustibles examined (e.g. hydrogen) is noteworthy. The effect is probably accountable on thermal grounds and may be interpreted as showing the contribution which the methyl bromide itself makes to the heat of reaction. It is known that it has a fairly large heat of combustion (184.7 kcal./mol.) (Heilbron 1934) and has been caused to ignite within narrow limits in air (13.5 to 14.5 %) by very powerful electrical ignition sources (Jones 1928). From the practical point of view, it is important to remember that proportions of methyl bromide below the extinguishing amount can render certain combustible gases more, rather than less inflammable, in the sense of lowering the lower limit of flame propagation.

Also included in table 2 are the mixture compositions represented by the 'peaks' of the several curves (maximum percentage of methyl bromide). It can be seen from these figures as well as from figure 3 that extinction of limits by methyl bromide is increasingly difficult in the order methane, carbon monoxide, ethylene, hydrogen. This is in accordance with previous experience in connexion with nitrogen and carbon dioxide as extinguishing agents (Coward & Jones 1938), and it will be noted that the order is that of the ratio upper/lower limit percentage of combustible in air.

In table 3 are the results, tabulated as in table 2, for systems incorporating the other extinguishing materials, namely difluorodichloromethane (freon 12) with hydrogen and with *n*-hexane, and carbon tetrachloride with methane. The latter system has been completely explored by Coward & Jones (1926) and our present results are in good agreement with theirs.

Appearance of flames. The variation in the character of the flame of each combustible in the presence of methyl bromide as the mixture composition passes round the boundary of the inflammable region, from the lower to the upper limit, will be described.

At the extremity of the lower limit side of the curve, in the absence of methyl bromide, the flame of each combustible except hydrogen was its own characteristic shade of pale blue. The flame front was a clear-cut dome but usually had a less distinct rear boundary. As methyl bromide was added, at the expense mainly of air, a luminous yellow blended with the lower limit flame. Shortly before the peak of the limit curve was reached, the yellow became sufficiently dense to obscure any other colour, and the flame increased in length to eight inches or more. Passing down the other side of the curve, increasing combustible at the expense mainly of methyl bromide, the flames remained luminous, and in the case of benzene, became sooty. When a mixture was outside this part of the curve it burned with a luminous flame in the atmosphere outside the tube. Within the curve, as the upper limit was approached, a more elaborate phenomenon occurred with ethylene, hexane, cyclohexane, benzene and coal gas. External burning was accompanied by a regular dome-shaped flame travelling up the tube. The expansion produced

by the partial combustion in the tube drove the products down to supply the external flame. When the internal flame went out at the top of the tube, the ensuing contraction drew in the secondary flame which then travelled irregularly a foot or two up the tube and dwindled away. Very near the upper limit, though the flames of benzene were luminous, those of hexane and cyclohexane were blue-violet. A little further from the limit, at 6.72% hexane for example, this translucent flame permitted the observation of a dull orange-red core, concentric with the flame-front, of perhaps half the diameter of the tube. This became involuted in a complicated scroll form as the flame proceeded.

TABLE 3. COMPOSITION OF MIXTURES (OTHER THAN THOSE INCORPORATING METHYL BROMIDE) AT LIMIT OF INFLAMMABILITY

incom- bustible vapour (%)	combustible %					
	hydrogen-freon 12		n-hexane-freon 12		methane-carbon tetrachloride	
	lower	upper	lower	upper	lower	upper
0	4.0*	73.8*	1.40	7.5	†	†
1	—	—	1.55	7.25	5.5	†
2	—	—	1.65	6.95	5.8	13.3
3	—	—	1.75	6.7	5.9	13.0
4	—	—	1.8	6.45	6.0	12.8
5	4	—	1.9	6.2	6.2	12.5
6	—	—	2.0	6.0	6.3	12.3
7	—	—	2.05	5.75	6.4	12.0
8	—	—	2.15	5.55	6.6	11.4
9	—	—	2.3	5.4	6.9	10.9
10	4.5	45	2.45	5.15	7.2	10.3
11	—	—	2.7	4.9	7.6	9.7
12	—	—	2.95	4.55	—	—
13	—	—	3.35	4.05	—	—
15	5.5	37	—	—	—	—
20	6	29	—	—	—	—
25	7	22	—	—	—	—
30	8	16	—	—	—	—
peak (%)						
combustible	10		3.6		8.3	
incombustible	35		13.5		12.0	

* From table 2.

† Not determined by the authors.

A special phenomenon was noted near the lower limit of hydrogen. (At the lower limit the flame was invisible and special measures were necessary for its detection, as described previously.) With just sufficient methyl bromide to make them visible, numbers of yellow spots of roughly 2 mm. diameter circulated rapidly within the rising dome. Sometimes the dome was striated with yellow and the spots appeared to drip from it. Phenomena of this kind have been previously observed by Coward & Brinsley (1914) and an explanation in terms of diffusion suggested by Harteck was supported by Goldmann (1929).

Flame-balls of a different character occurred with benzene near its upper limit. Three or four luminous balls of about 1 cm. diameter passed up the tube within a flame-front which, as with some of the more critical mixtures, was less well defined.

Safe mixtures. The chief contribution of this investigation is the complete delimitation of flame-propagating mixtures comprising some incombustible vapours and air together with representative combustible gases and vapours. A particular use of data of the kind obtained is to establish 'limiting safe mixtures' of the incombustible vapours with either air or combustible. Thus, if in diagrams of the kind shown in figure 3 a tangent is drawn from the origin to the extinction limit curve, the constant proportion of extinguisher to combustible thus represented is that of a limiting mixture of the two, which under the conditions of experiment cannot form explosive mixtures with air. Similarly, a tangent from the point combustible = 100 % represents a limiting proportion of extinguisher to air giving an atmosphere in which the combustible cannot propagate flame. The two mixtures thus defined have a certain practical significance and may be referred to as 'limiting safe mixtures' with respect to the third component. The content of incombustible vapour in such mixtures as determined from the present measurements are shown in table 4.

TABLE 4. LIMITING SAFE MIXTURES

combustible	incombustible	limiting safe percentage of incombustible vapour	
		with air	with combustible
hydrogen	methyl bromide	14.8	85
carbon monoxide	methyl bromide	7.6	28
methane	methyl bromide	5.1	45
ethylene	methyl bromide	12.0	85
coal-gas	methyl bromide	11.6	72
n-hexane	methyl bromide	7.2	80
cyclohexane	methyl bromide	7.6	78
benzene	methyl bromide	7.9	79
hydrogen	freon 12	39	78
n-hexane	freon 12	14.0	80
methane	carbon tetrachloride	13.1	60

Calculation of extinction limits for coal gas. Jones (1929) has shown how the effect of extinguishing materials upon the limits of many combustible gaseous mixtures can be approximately calculated using Le Chatelier's rule as extended by Coward (1919). This states that the limit for a gaseous mixture containing p_1 , p_2 , p_3 , etc. % of gases having limits of N_1 , N_2 , N_3 etc. is given by:

$$L = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \text{etc.}}$$

The rule applies both to lower and upper limits.

The method may be applied in the present work to calculate, for instance, the limits of a 1:1 coal gas-methyl bromide mixture as follows (see table 5).

TABLE 5. CALCULATION OF THE LIMITS FOR A 1:1
COAL GAS-METHYL BROMIDE MIXTURE IN AIR

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
con- stituent	percentage or parts per 100	parts of methyl bromide added	parts CO ₂ added	parts N ₂ added	parts combustible and diluent	percentage of diluted mixture	lower limit	upper limit
C ₂ H ₄	3.4	10.2	—	—	13.6	7.0	10.8	14.7
CO	12.3	2.5	—	—	14.8	7.6	18.4	31.8
H ₂	48.6	87.3	—	—	135.9	69.5	10.4	21.0
CH ₄	21.2 { 14.0 7.2	—	—	7.0	21.0	10.8	7.5	19.0
		—	2.7	—	9.9	5.1	7.4	17.4
CO ₂	2.7	—	—	—	—	—	—	—
N ₂	7.0	—	—	—	—	—	—	—
air	4.8	—	—	—	—	—	—	—
totals	100.0	100.0	2.7	7.0	195.2	100.0	—	—

The coal gas (100 parts by volume) may be sub-divided as in column (1) into combustible, air, nitrogen and carbon dioxide. Allocating methyl bromide (100 parts in all) to C₂H₄, CO and H₂ as in column (2), we get mixtures whose total volume is as shown in column (5), with limits derived from figure 3, as in (7) and (8). Allocating the 2.7 parts of CO₂ to some of the methane (column (3)) and the 7.0 parts of nitrogen to the rest (column (4)), and employing Jones' (1929) extinction limit curves, we get further mixtures whose volumes are shown in column (5), having limits as in (7) and (8). The percentage constitution of the diluted mixture (expressed in terms of combustible constituents and allocated diluents) is given in column (6). Using Le Chatelier's rule and allowing for 4.8% of air present in the coal gas, we have, from the figures in columns (6) and (7)

$$\text{lower limit} = \frac{100}{\frac{7.0}{10.8} + \frac{7.6}{18.4} + \frac{69.5}{10.4} + \frac{10.8}{7.5} + \frac{5.1}{7.4}} \times \frac{100}{95.2} = 10.6 \text{ \%}.$$

Employing the figures in columns (6) and (8), we have,

$$\text{upper limit} = \frac{100}{\frac{7.0}{14.7} + \frac{7.6}{31.8} + \frac{69.5}{21.0} + \frac{10.8}{19.0} + \frac{5.1}{17.4}} \times \frac{100}{95.2} = 21.5 \text{ \%}.$$

Using this method of calculation, other mixtures of coal gas and methyl bromide have been examined, with the results given in table 6. Comparative experimental limits are also given.

TABLE 6. COMPARISON OF CALCULATED AND MEASURED LIMITS OF COAL GAS

ratio: methyl bromide coal gas	calculated limits of diluted mixture		measured limits of diluted mixture	
	lower	upper	lower	upper
0	5.5	37.4	5.0	33.0
0.25	6.8	28.1	6.7	22.5
0.5	8.1	25.3	8.7	20.8
1.0	10.6	21.5	11.6	18.8
2.0	13.4	16.7	13.4	16.4
2.93	14.4	15.8	slightly beyond extinction limit	

It will be seen that, while agreement is good as regards the lower limit side of the curve, there is rather more divergence on the upper limit side. For most practical purposes, however, the errors involved (of the order of 10 %) would not be very serious, and it would generally be permissible to employ the method of calculation outlined both for upper and lower limits.

PRINCIPAL CONCLUSIONS

(1) A flow method for the determination of limits of flame propagation in complex gas mixtures has been developed and found to give satisfactory results less tediously than do static methods. In the form used it is only applicable where all components of the mixture are gaseous at atmospheric temperature.

(2) For mixtures of which one constituent is condensable a static method has been preferred, but special stirring arrangements have been found necessary.

(3) By means of the two methods described limits of flame propagation under standard conditions have been fully determined for ternary mixtures involving a number of combustibles mixed individually with methyl bromide and air. The combustibles were placed in the following order of increasing susceptibility to extinction by methyl bromide: hydrogen, ethylene, coal gas (composition as stated), benzene, cyclohexane, *n*-hexane, carbon monoxide and methane. Benzene, cyclohexane and *n*-hexane were approximately equally susceptible.

(4) Complete limits have also been delineated for mixtures with air of hydrogen and freon 12, *n*-hexane and freon 12; and methane and carbon tetrachloride.

(5) In some cases additions of methyl bromide appreciably *lowered* the lower limit of flame propagation, although in all cases a sufficient addition of the extinguisher always caused the upper and lower limits to converge to the point of coincidence. The initial lowering effect was not shown with freon 12 or carbon tetrachloride.

(6) The effect of methyl bromide upon the limits of the sample of (debenzolyzed) coal gas examined was calculated from data for hydrogen, ethylene, carbon monoxide and methane, by the use of Coward's extension of Le Chatelier's rule. Agreement with experimental results within about 10 %.

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Decay of isotropic turbulence in the initial period

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In a previous paper the authors described direct measurements of all the terms in the equation for the rate of change of mean square vorticity in isotropic turbulence. The present paper is concerned with developments arising from the earlier work and with the experimental verification of some recent theoretical investigations. The results of measurements of the turbulent intensity u' and of λ are presented; these establish that u'^{-2} and λ^2 are each proportional to the time of decay provided that the time is not too large. Within this initial period of the decay, the double and triple velocity correlation functions are found to maintain their form, i.e. to be self-preserving, for small values of the distance r between the two points at which the correlations are taken. For larger separations the double velocity correlation function changes its form slightly during decay and direct measurements of λ and of the integral scale L show that λ/L increases during the decay. Theoretical predictions about the shape of the correlation function, for limited ranges of r , at high and at low Reynolds numbers are compared with measurements.

Theory has shown that the above decay law cannot persist indefinitely, and the present experiments confirm that the decay law changes in the expected direction when the time is large. A division of the life-history of the turbulence into initial, transition and final periods is suggested; within the initial period, a classification based on the Reynolds number is also possible. Some speculations on the interpretation of the initial period are presented.

1. INTRODUCTION

In a previous paper (Batchelor & Townsend 1947—referred to hereafter as I) the authors have analyzed measurements of the rate of change of mean square vorticity in isotropic turbulence. It has been shown theoretically that two separate physical processes contribute to the change in the vorticity. The first process is an average extension of the vortex lines due to the random diffusive motion, giving a positive contribution to $d\omega'^2/dt$, where ω'^2 is the mean square of any vorticity component, which is directly related to the skewness of the probability distribution of the rate of extension of fluid elements aligned in any direction. The second process is a dissipation of the vorticity due to the effect of viscosity, and the contribution to $d\omega'^2/dt$ depends on the fourth derivative at the origin of the double velocity correlation function. Both of these contributions and the value of $d\omega'^2/dt$ itself were measured at different stages in the decay of the turbulence. The agreement made it clear that it is permissible to apply the theory of isotropic turbulence to the motion behind a grid in a uniform stream and that the measurements described were essentially correct.

The plan of measuring all terms in an equation derived from the property of isotropy was also adopted for the energy balance. This equation contains only the mean energy per unit mass, $\frac{3}{2}u'^2$, and the dissipation length parameter λ , in addition to the independent variable t representing time. u'^{-2} and λ^2 were found to increase linearly with t , so that the Reynolds number $R_\lambda = u'\lambda/\nu$, was approximately constant for the range of grid Reynolds numbers and decay times used in the experiments. Once again the measurements were found to satisfy the equation.

Another result which emerged from the experiments was that there is some measure of self-preservation of shape of the functions $f(r)$ and $k(r)$ which describe the double and triple velocity correlations. f and k were found to be functions of the variable r/λ alone, not depending directly on t , so far as terms up to the fourth and third degree respectively in their expansions in powers of r are concerned. This property of self-preservation of the correlation functions is intimately related to the law of energy decay. One of us has therefore made a full theoretical analysis (Batchelor 1948—to be referred to as II) of the consequences of various kinds of self-preservation hypotheses under different Reynolds number conditions, and it has been found possible to make a number of predictions.

The present paper is in a direct sequence with the work of I and II. Its first aim is to determine the validity of the energy decay law reported in I over as wide a range of grid Reynolds numbers and decay times as the wind tunnel in the Cavendish Laboratory permits. The second aim is to examine the double velocity correlation at different decay times in order to see the extent of the property of self-preservation of shape. Finally, as many of the theoretical deductions of II as come within the scope of the measurements will be put to the test.

The measurements of the various statistical quantities associated with the turbulence have been made wholly with a hot-wire anemometer and wherever possible,

direct measurements obtained by a suitable electrical analysis of the wire output have been preferred. In this way direct measurements of u' , λ , $k_0''\lambda^3$ and $f_0^{1/2}\lambda^4$ as described in I, and of $\int_0^\infty f dr$, $g(r)$ and $k(r)$ have been made. Details of the methods are described fully in a separate paper by one of us (Townsend 1947). The wind tunnel used in the experiments is situated in the Cavendish Laboratory, Cambridge, and has been described in I. As is customary, the time of decay in the idealized problem of homogeneous isotropic turbulence will be identified with the time x/U which has elapsed since any point distance x from the turbulence-producing grid and moving with the mean stream was at the grid.

2. NOTATION TO BE USED

u'^2 = mean square fluctuation of any velocity component.

$\omega'^2 = 5u'^2/\lambda^2$ = mean square fluctuation of any vorticity component.

x = distance from the grid.

M = periodic spacing of the turbulence-producing grid.

d = diameter of the rods comprising the grid.

U = velocity of the uniform stream relative to the grid.

$R_M = UM/\nu$: Reynolds number associated with the grid.

$f(r)$, $g(r)$, $k(r)$: double and triple velocity correlation coefficients in the sense used in I and first defined by v. Kármán & Howarth (1938).

$$\lambda^{-2} = -\left(\frac{\partial^2 f}{\partial r^2}\right)_{r=0} = -\frac{1}{2}\left(\frac{\partial^2 g}{\partial r^2}\right)_{r=0}.$$

$$\psi = r/\lambda.$$

$R_\lambda = u'\lambda/\nu$: Reynolds number of the turbulence.

$L = \int_0^\infty f dr = 2 \int_0^\infty g dr$: integral scale of the turbulence.

$s = -k_0''\lambda^3 = -\left(\frac{\partial u}{\partial x}\right)^3 \left[\left(\frac{\partial u}{\partial x}\right)^2\right]^{-1}$: skewness (with sign reversed) of the probability distribution of the rate of extension in any direction.

l = maximum value of r for which self-preservation of f , g and k occurs during the initial period.

C_D = drag coefficient of grid.

3. THE SIGNIFICANCE OF THE 'INITIAL PERIOD OF DECAY'

As a result of the experiments described in I and the theoretical analysis in II, it has become clear that there are two distinct phases in the life-history of isotropic turbulence produced by a grid, with a transitional phase connecting them. The phase which may be termed the *initial period of decay* is characterized by the existence of the energy decay law

$$u'^{-2} \propto t, \quad \lambda^2 = 10\nu t. \quad (3.1)$$

The measurements reported in I were made behind several grids ($M = 1.27, 2.54$ and 5.08 cm.) over ranges which lay within the limits $x/M = 20$ to $x/M = 130$ and the turbulence was in every case evidently within the initial period of decay. The range $x/M < 20$ is of course excluded from the system of classification since the turbulence takes a little time to become uniform (in the lateral direction) and isotropic. It remains to be seen whether it is possible to define an initial period of decay by the laws (3.1) for all values of the grid Reynolds number. The experiments of I covered the range $R_M = 5.5 \times 10^3$ to 4.4×10^4 and experiments to be described herein confirm the validity of the laws (3.1) in the initial period of decay for values of R_M at least down to 600.

Now in II it was shown theoretically that the only possible regime at very large times of decay is one in which the correlation functions are completely self-preserving and the law of energy decay is $u'^{-2} \propto t^{\frac{1}{2}}, \quad \lambda^2 = 4\nu t.$ (3.2)

The double velocity correlation function has the form

$$f(r) = e^{-r^2/2\lambda^2} \quad (3.3)$$

and the effect of the triple correlation is negligible. The authors propose that this phase be termed the *final period of decay*. There will also be a *transitional period of decay* when the mechanics of the turbulent motion is changing in type. As yet there is no definite information about the magnitudes of the decay times defining the extent of the different phases, but the experiments described below and others previously reported fix upper limits to the initial period for a few values of R_M .

It is possible to make, for the initial period of this fundamental division of the life-history of the turbulence into three phases, an equally fundamental classification depending on the magnitude of the Reynolds number. The basis for the classification lies in the relative effects on the turbulence of the inertia and viscous terms of the Navier-Stokes equations and a convenient analytical criterion can be obtained from the equation for decay of mean square vorticity. It was seen in I that this equation can be written as

$$\frac{3\sqrt{5}}{14} \frac{d\omega'^2}{dt} = \frac{s}{2} \omega'^3 - \frac{f_0^{IV} \lambda^4}{R_\lambda} \omega'^3. \quad (3.4)$$

Using the decay law (3.1) appropriate to the initial period, the left side becomes $-\frac{30}{7} \frac{\omega'^3}{R_\lambda}$, and the equation reduces to

$$\omega'^3 \left(-\frac{30}{7} \frac{1}{R_\lambda} = \frac{s}{2} - \frac{f_0^{IV} \lambda^4}{R_\lambda} \right). \quad (3.5)$$

The first term on the right side is derived from the inertia terms of the Navier-Stokes equations and represents the creation of mean square vorticity due to the diffusive increase in length of vortex lines. The second term on the right side represents the destruction of vorticity due to viscosity. Thus, the ratio of the viscous to the inertia effect is

$$\frac{2 f_0^{IV} \lambda^4}{s R_\lambda} = 1 + \frac{60}{7s} \frac{1}{R_\lambda}. \quad (3.6)$$

The experiments of I established for the initial period of decay and

$$0.5 \times 10^4 < R_M < 4.5 \times 10^4$$

that the skewness factor s is approximately an absolute constant with a value close to 0.39. Hence the factor which governs the relative importance of the viscous and inertia effects on the rate of change of mean square vorticity is

$$1 + \frac{22}{R_\lambda}. \quad (3.7)$$

The number R_λ clearly plays a fundamental role in the theory of isotropic turbulence and the authors propose to call it the Reynolds number of the turbulence. Since R_λ is constant during the initial period of the decay, the value of R_λ is a convenient and significant index to the type of turbulence occurring throughout that period. Three roughly separate regimes depending on the magnitude of R_λ can be distinguished. The regime of large Reynolds numbers of turbulence is such that $22/R_\lambda \ll 1$ and the contributions to $d\omega'^2/dt$ from the viscous and inertia terms are approximately equal and opposite. At intermediate Reynolds numbers the factor $22/R_\lambda$ is of order unity and the ratio of the two contributions to $d\omega'^2/dt$ is significantly different from unity. Finally, at small Reynolds numbers of turbulence, $22/R_\lambda \gg 1$, and the effect of the triple correlations on $d\omega'^2/dt$ is negligible compared with the viscous dissipation.

Each of these three regimes has its own body of theory. The existence of large Reynolds numbers of turbulence is basic to the theory of locally isotropic turbulence, first put forward by Kolmogoroff (1941) and developed more recently by one of us (Batchelor 1947). There is no need to describe here the results of this theory except to remark that it predicts that the skewness factor s is an absolute constant, and the experimental evidence (see I) for this result in the range of intermediate Reynolds numbers thus shows that there is some overlapping of the Reynolds number categories. There are other results of the theory, e.g. concerning the form of the function $f(r)$, which do not appear to be true at intermediate Reynolds numbers. There is as yet insufficient evidence to be certain that the energy decay law (3.1), which has been taken to define the initial period of decay, continues to hold as R_λ becomes large (the measurements described below confirm it as far as $R_\lambda = 60$), nor is this decay law necessary to the theory of locally isotropic turbulence, so that this part of the classification is provisional.

No unqualified deductions about the turbulence at intermediate Reynolds numbers have been made, but a few results have been obtained in II on the assumption of limited self-preservation of the correlation functions, i.e. that f and k are functions of r/λ only, provided $0 \leq r < l$, where l is an unspecified length which is not too large. There were found to be two possible ways of proceeding from this assumption. According to the first method of solution the law of energy decay is given by (3.1), whereas the second method gives a different decay law which asymptotes to (3.1)

at t increases. Since there is no means of predicting the rate of approach to (3.1), measurement of the energy decay law is not sufficient to choose between the two solutions. However they make different predictions about the correlation functions and the evidence presented below is sufficient to show that one solution is correct. When R_λ is small, it has been found possible (see II) to predict the form of the function $f(r)$ for as large a range of r as $f(r)$ is self-preserving during decay.

The experiments reported in I and those to be described below are concerned largely with the initial period of decay and with intermediate Reynolds numbers of turbulence. For three values of R_M the measurements have been made over a decay range which is sufficiently large to extend beyond the initial period and into the transitional period. Some results have been obtained under the conditions of large and small Reynolds numbers of turbulence and these show quite good agreement with the appropriate theoretical deductions.

4. RÉSUMÉ OF THEORETICAL RESULTS TO BE EXAMINED

The deductions which will be compared with experiment are set out in the following table. Reference should be made to the papers quoted for other deductions, from the same hypotheses, which do not lie within the scope of the experiments.

conditions	hypothesis	deductions
<i>initial period of decay</i>		
$\frac{22}{R_\lambda} \ll 1$	Kolmogoroff's similarity hypotheses	(a) $g(r) = 1 - \frac{1}{2}C\left(\frac{15}{R_\lambda} \frac{r}{\lambda}\right)^{\frac{1}{2}}$, for $r \ll L$, where C is an absolute constant (b) $k_0'' \lambda^2$ and $f_0'' \lambda^4$ are constant if R_λ is constant during decay (c) s is an absolute constant } see I for verification
$\frac{22}{R_\lambda} = O(1)$	$f(r) \equiv f(r/\lambda)$, $k(r) \equiv k(r/\lambda)$, for $0 \leq r < l$	either (a) $R_\lambda = \text{constant during decay}$, and $f'' + f' \left(\frac{4}{\psi} + \frac{5\psi}{2} \right) + 5f + \frac{1}{2} R_\lambda \left(k' + \frac{4}{\psi} k \right) = 0, \quad \text{for } 0 \leq r < l$ (dashes denote differentiation with respect to ψ), or (b) an energy decay law which asymptotes to $R_\lambda = \text{constant}$, and $f'' + \frac{4}{\psi} f' + \left(\frac{5}{2} + \frac{7}{12} s R_\lambda \right) \psi f' + 5f = 0, \quad \left. \begin{array}{l} k' + \frac{4}{\psi} k = \frac{7}{6} s \psi f' \end{array} \right\} \text{ for } 0 \leq r < l$
$\frac{22}{R_\lambda} \gg 1$	$f(r) \equiv f(r/\lambda)$, for $0 \leq r < l$	$R_\lambda = \text{constant}$, and $f'' + f' \left(\frac{4}{\psi} + \frac{5\psi}{2} \right) + 5f = 0, \quad \text{for } 0 \leq r < l$
<i>final period of decay</i>		
—	—	$u'^2 \propto t^{\frac{1}{2}}, \quad \lambda^2 = 4\nu t \quad \text{and} \quad f(r) = e^{-r^2/4\lambda^2}$

5. MEASUREMENTS OF u' AND λ

Measurements of the quantities u' and λ which occur in the energy equation, viz.

$$\frac{du'^2}{dt} = -\frac{10\nu u'^2}{\lambda^2}, \quad (5.1)$$

were made at various distances from a turbulence-producing grid. Four similarly shaped biplane grids constructed of circular cylinders of diameter $3M/16$ were used; the values of M were 5.08, 2.54, 1.27 and 0.635 cm. Measurements of λ were corrected for finite wire-length. The data are presented in figures 1 to 4. These diagrams contain the results described in I, together with new results for the smallest grid, and for the larger grids at different wind speeds. They summarize all the authors' experiments concerning the decay law (3.1), which is regarded as a characteristic of the initial period of decay.

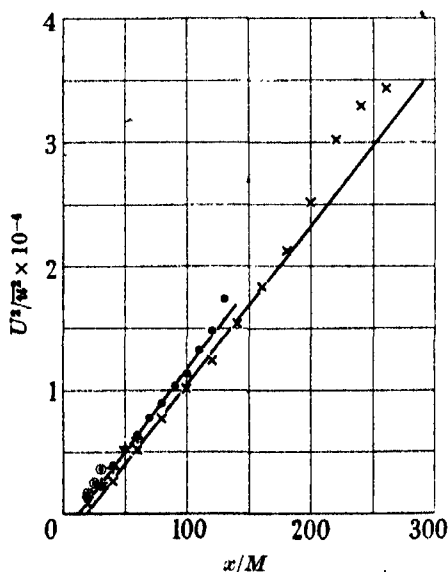


FIGURE 1. $\frac{u'^2}{U^2}$ vs. $\frac{x}{M}$ ($U = 643$ cm.sec. $^{-1}$).

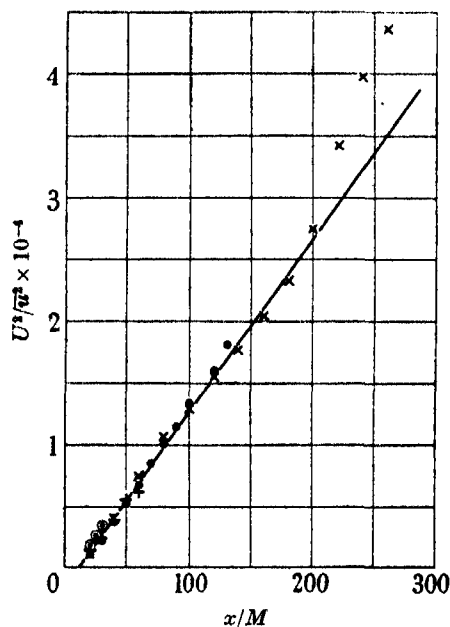


FIGURE 2. $\frac{u'^2}{U^2}$ vs. $\frac{x}{M}$ ($U = 1286$ cm.sec. $^{-1}$).

$\times$ $M = 0.635$ cm. $\bullet$ $M = 1.27$ cm. $+$ $M = 2.54$ cm. $\circ$ $M = 5.08$ cm.

It will be seen from figures 1, 2 and 3 that most of the measurements of U^2/u'^2 lie about a linear variation with x/M ; only at the large values of x/M obtained with the smallest mesh ($M = 0.625$ cm.) do the points depart appreciably from a straight line. It is thus possible to write

$$\frac{U^2}{u'^2} = \alpha \left(\frac{x}{M} - \frac{x_0}{M} \right) \quad (5.2)$$

for an initial range of values of x/M , where α and x_0 are constants. The energy equation (5.1) then requires

$$\lambda^2 = \frac{10\nu}{U}(x - x_0) = \frac{10M^2}{R_M} \left(\frac{x}{M} - \frac{x_0}{M} \right); \quad (5.3)$$

the rather curious but well-known result that λ^2 depends only on the viscosity and time of decay—depending not at all on M or U directly—is a consequence of any decay law which makes u'^2 vary as some power of x or t . In the plot of λ^2 vs. x in figure 4, lines are drawn with slope $10\nu/U$ and they represent well the experimental

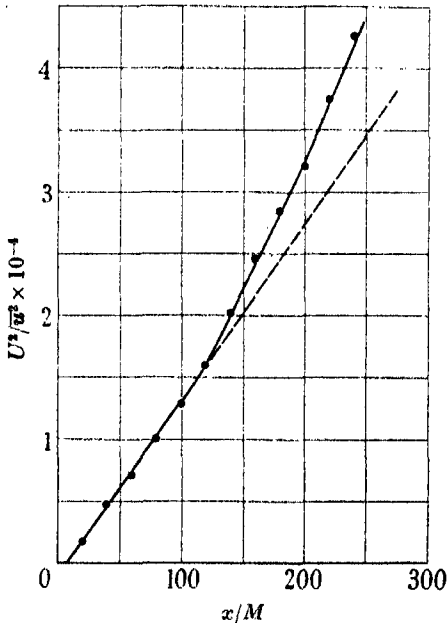


FIGURE 3. $\frac{u'^2}{U^2}$ vs. $\frac{x}{M}$

($U = 150$ cm.sec. $^{-1}$, $M = 0.635$ cm.)

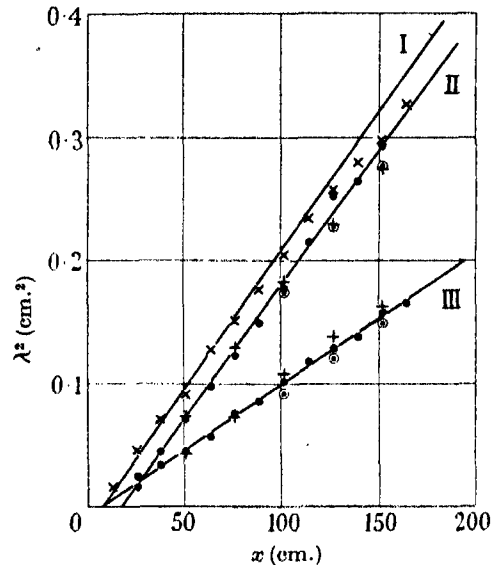


FIGURE 4. λ^2 vs. x

Curves I and II, slope = 2.26 cm. = $\frac{10\nu}{U}$
($U = 643$ cm.sec. $^{-1}$).

Curve III, slope = 1.13 cm. = $\frac{10\nu}{U}$
($U = 1286$ cm.sec. $^{-1}$).

$\times$ $M = 0.635$ cm. $\bullet$ $M = 1.27$ cm.
 $+$ $M = 2.54$ cm. $\circ$ $M = 5.08$ cm.

variation, with the exception of the range $x/M > 180$ obtained with the smallest mesh. The experimental points would in no case be represented better by a straight line of slope more than 10 % different from $10\nu/U$. Thus the power of $(x - x_0)$ which represents the variation of u'^{-2} in these experiments does not differ from unity by more than 10 %.

The energy equation also requires the extrapolations of U^2/u'^2 and λ^2 to vanish at the same value of x . This virtual origin at $x = x_0$ represents the position at which

the turbulence is effectively created with infinite energy. Values of x_0 given by the straight lines best fitting observations of U^2/u'^2 and λ^2 (in the case of λ^2 the slope of the lines was taken as $10\nu/U$ and only the position was varied to improve the fit) are set out in table 1 and are approximately in accord.

TABLE 1. MEASUREMENTS OF u' AND λ BEHIND SIMILAR GRIDS

M (cm.)	U (cm.sec. ⁻¹)	R_M	$\left(\frac{x}{M}\right)_{U/u'=0}$	$\left(\frac{x}{M}\right)_{\lambda=0}$	$\frac{d(U^2/u'^2)}{d(x/M)}$	R_λ
0.635	643	0.28×10^4	20	12	128	14.4
1.27	643	0.55	12	13	132	20.3
2.54	643	1.10	10	7	130	28.7
5.08	643	2.21	3	5	—	41
0.635	1286	0.55	9	—	140	20.3
1.27	1286	1.10	15	5	151	28.7
2.54	1286	2.21	8	3	126	41
5.08	1286	4.42	6	3	—	58

Many investigators in the past have found that U^2/u'^2 when plotted as a function of x/M appears to be approximately independent of U and M for similar grids. The present measurements support this conclusion. Apart from the small change in virtual origin of the turbulence with R_M , there is a little variation (apparently random) in the slope factor α as shown in table 1.

$$\text{From (5.2) and (5.3)} \quad R_\lambda = \frac{u'\lambda}{\nu} = \left(\frac{10R_M}{\alpha} \right)^{\frac{1}{2}}, \quad (5.4)$$

and R_λ is constant during the initial period of decay. Knowledge of α for the types of grids commonly used in experiments therefore enables R_λ to be calculated for given values of U and M and as has already been seen, the value of R_λ is a significant index to the state of the turbulence. The data in table 1 show that the average value of α for the various values of M and U is 134 (no slope factor is deduced from measurements with $M = 5.08$ cm. since these could only be made over a very small range of values of x/M); this figure is appropriate to biplane grids for which the ratio of rod spacing M to diameter d is $\frac{1}{3}$. The values of R_λ calculated from (5.4) with $\alpha = 134$ are shown in the last column of table 1. They represent well the values of $u'\lambda/\nu$ obtained from the measurements of u' and λ except for the smallest values of x/M where the influence of the disparities in the virtual origins appropriate to the U^2/u'^2 and λ^2 curves is strong.

Measurements behind the grid of smallest M extended beyond the range of validity of the decay law (5.2). For $x/M > 180$ the measured values of U^2/u'^2 and λ^2 at all speeds show a rate of energy decay which is more rapid than that which holds in the initial period. The extent of the initial period of decay will probably depend on the grid Reynolds number and on the initial correlation functions created by the grid, but the tunnel available to the authors is too short to allow any systematic results

to be established. There appears to be a slow diminution in the extent of the initial period as R_M increases (see table 2 below).

Dryden (1943) has discussed the measurements of u' published by several authors and has compared them with the decay law (5.2). He finds moderately good agreement in all cases, particularly at the smaller values of x/M . In some cases the deviations found by Dryden can be interpreted as the beginning of the transitional period of decay. This is almost certainly true of v. Kármán's data. Von Kármán (1938) has presented measurements of u' behind four grids of the woven wire type with different values of M/d which, when plotted in the appropriate manner, show that U^2/u'^2 is initially proportional to x/M , but in some cases increases more rapidly for larger values of x/M . The essential features of v. Kármán's data are set out in table 2 for comparison with the measurements given by the authors. The point at which the linear decay law ceases to be valid is necessarily rather indefinite and the estimates given in the table are only useful as a guide.

TABLE 2. GRIDS OF DIFFERENT SHAPE

source	M (cm.)	M/d	UM/ν	upper limit to extent of initial period	$\frac{d(U^2/u'^2)}{d(x/d)}$ in initial period	$C_D \left[\frac{d(U^2/u'^2)}{d(x/M)} \right]$
v. Kármán	1.27	2.16	1.00×10^4	$x/M > 210$	7.0	128
v. Kármán	1.27	4.76	1.41	$x/M = 220 (?)$	3.1	106
v. Kármán	1.27	4.76	1.00	137	20.8	96
v. Kármán	1.27	6.04	2.00	113	23.6	90
v. Kármán	1.27	6.04	1.00	113	23.6	90
v. Kármán	1.27	11.6	2.00 } 1.00 }	no discernible initial period		
present authors	0.635	5.33	0.064	120	average for different	average for different
present authors	0.635	5.33	0.28	180	M and U	M and U
present authors	0.635	5.33	0.56	200	(see table 1)	= 105
					= 25.1	

It has already been mentioned that the slope factor α of equation (5.2) appears to be independent of R_M for similar grids. It must thus be wholly determined by the characteristics of the grid which produces the turbulence. Two characteristics of the grid are relevant. The first is the drag per unit area, since it is the work done against this force which governs the amount of turbulent energy created by the grid. The second is the geometry of the grid, since this determines the length characteristics of the initial turbulence. These grid effects may be taken into account by writing

$$\frac{U^2}{u'^2} = \frac{\beta}{C_D} \left(\frac{x}{M'} - \frac{x_0}{M'} \right), \quad (5.5)$$

where β is an absolute constant, $C_D \cdot \frac{1}{2} \rho U^2$ is the drag of unit cross-sectional area of the grid and M' is an effective unit of length. M' will depend more on the spacing of the grid elements than on their dimensions.

Now when M/d is large, the drag of each grid element will be unaffected by the presence of its neighbours and C_D is proportional to d/M . This explains v. Kármán's observation that his measurements of U^2/u'^2 for the various grids came closer to coincidence when plotted against x/d rather than against x/M . However, table 2 shows there is still considerable variation in the value of $\frac{d(U^2/u'^2)}{d(x/d)}$ for the smaller values of M/d where the interference drag of the grid elements is appreciable. There have been many measurements of the drag of square grids of parallel circular cylinders in the past, and the formula which seems to represent the data best is*

$$C_D = \frac{\frac{d}{M} \left(2 - \frac{d}{M}\right)}{\left(1 - \frac{d}{M}\right)^4}. \quad (5.6)$$

Using this formula, the values of C_D for the grids used by v. Kármán and the present authors have been estimated and the last column of table 2 shows that the values of $C_D \left[\frac{d(U^2/u'^2)}{d(x/M)} \right]$ are more nearly constant than those of $\frac{d(U^2/u'^2)}{d(x/d)}$. The agreement is now as good as could be expected in view of the uncertainty of the estimates of C_D and of the difficulty in making absolute measurements of u' ; hence, so far as can be told from the data in table 2, the effective mesh length M' in (5.5) is approximately equal to M . β is given approximately by the average of the figures in the last column, with a total weight of unity for each group of readings which apply to one value of M/d , and (5.5) can be written approximately as

$$\frac{U^2}{u'^2} = \frac{106}{C_D} \left(\frac{x}{M} - \frac{x_0}{M} \right). \quad (5.7)$$

Further measurements are necessary before this relation can be applied with confidence to grids of arbitrary shape.

The formula (5.7) can also be written as

$$\frac{u_0'^2}{u'^2} = \frac{t}{t_0}, \quad (5.8)$$

which is more appropriate to the idealized problem of the decay of strictly homogeneous turbulence, since the factors related to the grid do not occur explicitly. $u_0'^2$ is the initial intensity of the turbulence created by the grid and is proportional to $C_D U^2$. t_0 is the time interval between the instant at which the extrapolated intensity would have been infinite and the initial instant at which it is $u_0'^2$. Evidently t_0 is proportional to M/U , as would be expected on the grounds that M and U are the factors most relevant to a time scale.

* See L. F. G. Simmons & C. F. Cowdray, Measurements of the aerodynamic forces acting on porous screens, *Aero. Res. Coun. Unpub. Rep.* 8920 (1945).

6. MEASUREMENTS OF $g(r)$ (a) *Limited self-preservation of $g(r)$*

The two double velocity correlation functions $f(r)$ and $g(r)$ are related by the continuity condition, viz.

$$g = f + \frac{r}{2} \frac{\partial f}{\partial r} \quad (6.1)$$

and a measurement of either is sufficient to determine the general double velocity correlation. Measurement of the lateral correlation is more convenient practically, and most of the $g(r)$ curve has been determined at a number of distances downstream from the grid for several values of U and M . Figures 5 to 8 exhibit the results. Each diagram refers to a single value of R_M and shows a family of curves of g against r/λ , each member of the family referring to a particular stage in the decay. The relative positions of the curves are sensitive to the values of λ at each value of x/M and so λ has been obtained from a smoothed experimental curve of λ against x/M . The method of measurement of g was less accurate at small values of r , but the parabolic variation of g near the origin has previously been verified and may be assumed with confidence.

Accurate self-preservation of the function g seems to hold for r/λ lying between 0 and some figure of the order of 1, the range being larger at the higher Reynolds numbers. A more satisfactory method of determining the extent of the self-preserving property is to measure directly the derivatives of $f(r)$ at $r = 0$ at different distances from the grid. Measurements of $f_0^{(v)} \lambda^4$, described in I, were found to be approximately constant during the decay. However, as mentioned in that paper, direct measurement of higher derivatives presents considerable difficulties.

The chief feature of each family is that, apart from within the self-preserving region, the values of r/λ corresponding to a given value of g decrease with increase of x/M . That is to say, outside the self-preserving region, the curves $g(\psi)$ of any family have roughly the same shape but contract laterally as x/M increases. Note however, that the change with x/M in the outer parts of the curves cannot be described exactly by such a contraction, for each curve must satisfy the identity

$$\int_0^\infty \psi^4 g(\psi) d\psi = 0 \quad (6.2)$$

deduced from (6.1). The correlation functions f and g would be expected to diminish in absolute value at large values of r/λ with increase of x/M , since it was shown in II that

$$u'^2 \int_0^\infty f r^4 dr = \Lambda,$$

is constant during decay, and consequently, from (6.1),

$$\int_0^\infty \psi^4 f(\psi) d\psi = -\frac{2}{3} \int_0^\infty \psi^4 g(\psi) d\psi = \frac{\Lambda}{u'^2 \lambda^5}, \propto t^{-1}. \quad (6.3)$$

This relation is clearly consistent with a tendency for the curves of a family to contract slightly as t , or x/M , increases, since the absolute value of g diminishes with increase of r/λ when r/λ is large.

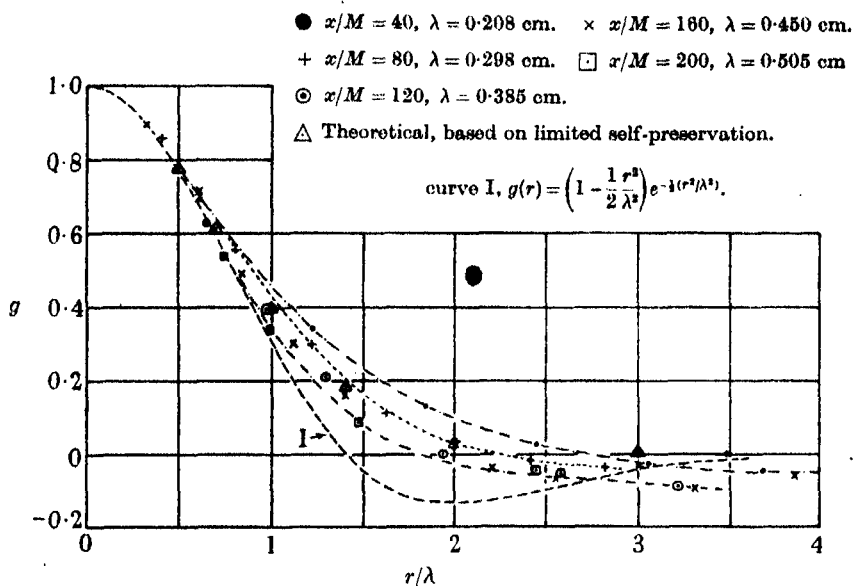


FIGURE 5. Transverse correlation. $U = 643$ cm.sec.⁻¹, $M = 0.635$ cm.,

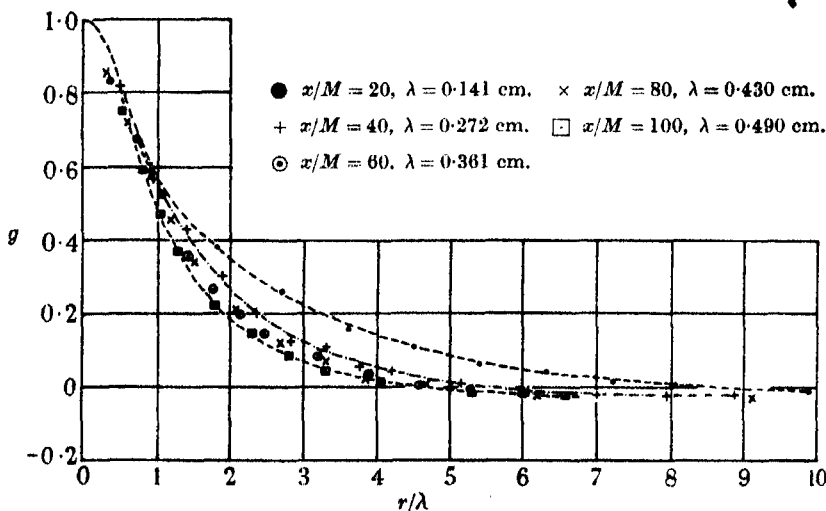


FIGURE 6. Transverse correlation. $U = 643$ cm.sec.⁻¹, $M = 1.27$ cm.

It follows from these considerations that the area $\int_0^\infty g(\psi) d\psi$ diminishes with x/M , and thence that the integral scale $L, = \int_0^\infty f dr = 2 \int_0^\infty g dr$, increases with x/M less rapidly than does λ . This is borne out by direct measurements of L , the

results of which are shown in figures 10 and 11. Figure 10 shows $(L/M)^2$ plotted against x/M and on the basis of similar evidence Dryden (1943) has represented the experimental variation by a straight line. At best this is an approximation, since

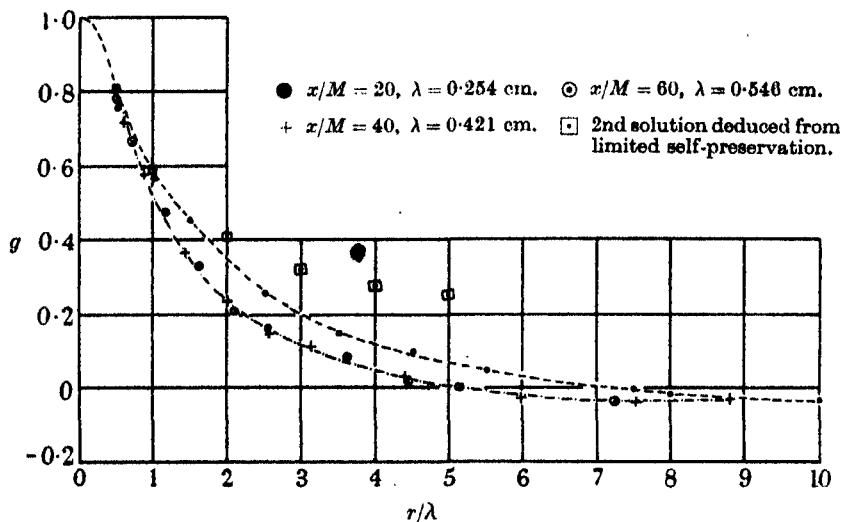


FIGURE 7. Transverse correlation. $U = 643$ cm.sec. $^{-1}$, $M = 2.54$ cm.

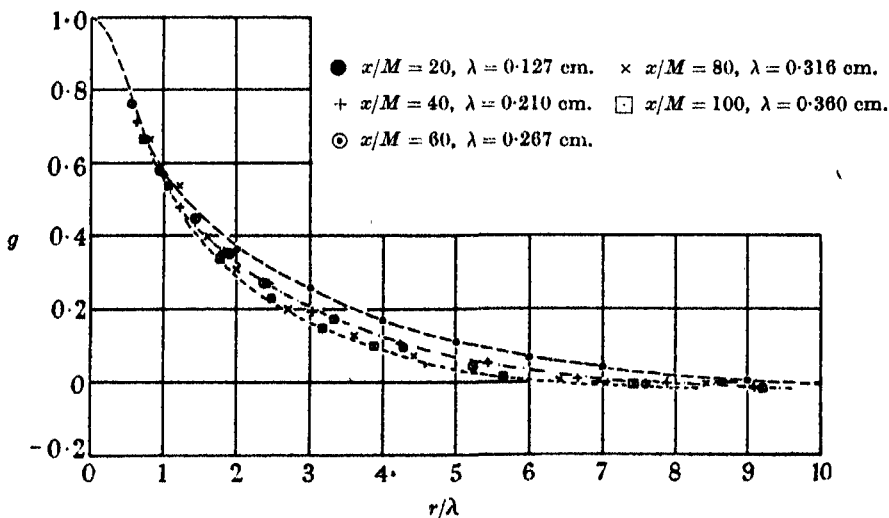


FIGURE 8. Transverse correlation. $U = 1286$ cm.sec. $^{-1}$, $M = 1.27$ cm.

an exact linear variation would imply complete self-preservation. It is doubtful whether the variation of L with x obeys any simple power law. Figure 11 shows that λ/L increases most rapidly when x/M is small, and is consistent with figures 5 to 8. The value of λ/L in the final period of decay is found from (3.3) to be $\sqrt{(2/\pi)} = 0.80$,

and this is presumably the asymptote toward which the curves of figure 11 ultimately tend. A point of interest about the measurements of scale is that at the virtual origin of the turbulence, L/M is in the neighbourhood of 0.3 or 0.4.

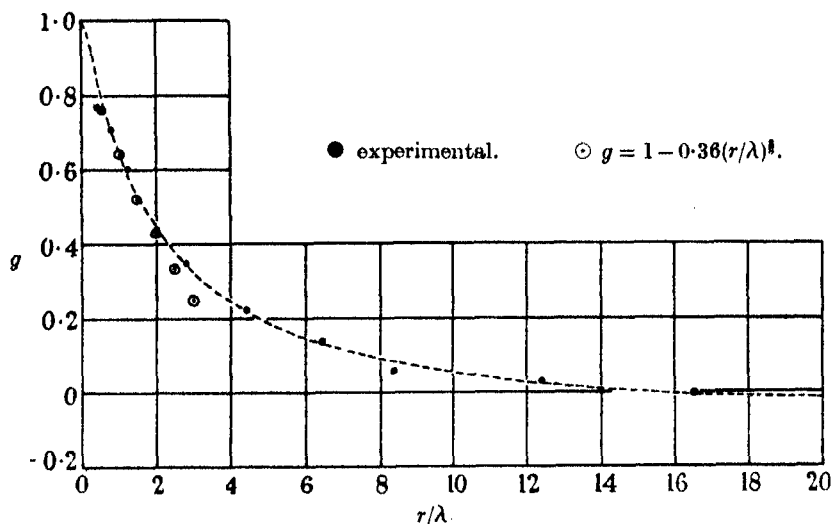


FIGURE 9. Transverse correlation. $U = 1286$ cm.sec. $^{-1}$, $M = 5.08$ cm.
 $x/M = 20$, $\lambda = 0.316$ cm.

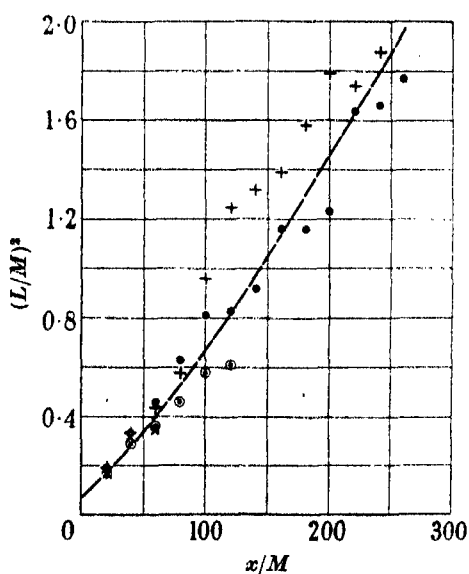


FIGURE 10. Variation of scale during decay.

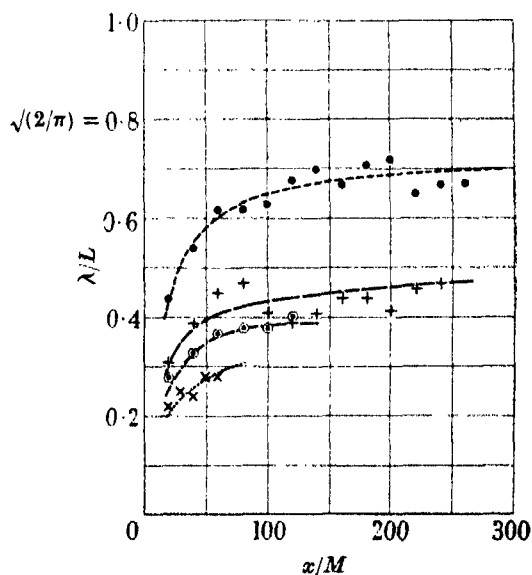


FIGURE 11. λ/L vs. x/M .

● $R_M = 2810$. + $R_M = 5620$. ○ $R_M = 11250$. × $R_M = 22500$.

(b) *Predictions about g*

It was stated in II that measurements of g would help to establish the validity of one of the two alternative deductions from the postulate of limited self-preservation. The first solution, which gives a decay law such that R_λ is constant, makes no prediction about f or g , but the second solution gives a decay law such that R_λ tends to a constant together with the equation

$$f'' + \frac{4}{\psi} f' + \left(\frac{5}{2} + \frac{7}{12}sR_\lambda\right) \psi f' + 5f = 0 \quad (r < l), \quad (6.4)$$

where s is the skewness factor found in I to be an absolute constant close to 0.39, and R_λ in (6.4) represents the asymptotic value. The solution of (6.4) can be obtained in the form of an indefinite integral and has been computed for a number of the values of R_λ at which measurements of g were made. Comparison of the measured and calculated curves of g as a function of ψ for one value of R_λ is shown in figure 7 and is typical of comparisons at other Reynolds numbers. The agreement is not good, particularly when it is recalled that one of the constants in the solution was chosen to make $f_0'' \lambda^4$ agree with the value found by direct measurement (see I and II). Thus there is reason to reject the second of the two alternative deductions from limited self-preservation and further evidence given in § 7 shows that the first solution is valid.

(c) *Solution for small values of R_λ*

A deduction from the postulate of limited self-preservation which is consistent with either of the solutions just mentioned is that, in the initial period of decay,

$$f'' + f' \left(\frac{4}{\psi} + \frac{5\psi}{2} \right) + 5f = 0 \quad (6.5)$$

for $r < l$, when R_λ is sufficiently small. This equation describes the effect of viscosity on the smaller eddies of the turbulence in the initial period. The solution which makes $f = 1$ at $\psi = 0$ is

$$f(\psi) = \frac{3}{2} e^{-\frac{1}{2}\psi^2} \int_0^1 \tau^{\frac{1}{2}} e^{\frac{1}{2}\psi^2 \tau} d\tau. \quad (6.6)$$

The corresponding solution for $g(\psi)$ can be obtained from (6.1) and numerical values are shown in figure 5. This figure also contains the measured values of g at the lowest Reynolds number used in the correlation experiments. The agreement is good for $r/\lambda < 1.5$, except perhaps for the measurements close to the grid where accurate values of λ are difficult to obtain. The measured values of g become negative in the neighbourhood of $r/\lambda = 2$ whereas the solution (6.6) is everywhere positive; this sets an upper limit to the region of self-preservation.

Some departure from the solution (6.6) at $x/M = 200$ might be expected, since it has already been found that this position is slightly outside the initial period. The solution appropriate to the final period is obtained from (3.3) and (6.1) as

$$g = \left(1 - \frac{1}{2} \frac{r^2}{\lambda^2} \right) e^{-(r^2/2\lambda^2)} \quad (6.7)$$

and this curve is shown in figure 5 for comparison. The departures from the solution (6.6) at large values of x/M are in the direction to be expected from an approach to (6.7).

The value of R_λ for the measurements in figure 5 was 14.4, and the range of 'small' Reynolds numbers of turbulence such that the inertia forces play no part in the determination of the correlation function g (or f) therefore has its upper limit near this value. However, at this value of R_λ the ratio of the viscous to the inertia effect in the balance of mean square vorticity is only 2.5, so that the inner region of the correlation curve must be less sensitive to the effect of the inertia forces than the vorticity.

(d) *Large Reynolds numbers*

The present experiments were not designed to make possible a comparison of Kolmogoroff's theory of local isotropy with experiment, but the single measurement of the function g made at $R_M = 4.42 \times 10^4$ (see figure 9) may be used for this purpose. R_λ is here equal to 58 so that the ratio of the viscous to the inertia effect in the balance of vorticity is equal to 1.38. The theory predicts (Kolmogoroff 1941; Batchelor 1947) that

$$g(r) = 1 - \frac{2}{3}C \left(\frac{15r}{R_\lambda \lambda} \right)^{\frac{1}{2}} \quad (6.8)$$

provided $\eta \ll r \ll L$, where C is an absolute constant, η is a length of order $\lambda/\sqrt{R_\lambda}$ and L is the integral scale of turbulence. The curve of this shape which appears to fit the observations quite well is

$$g(r) = 1 - 0.36 \left(\frac{r}{\lambda} \right)^{\frac{1}{2}}.$$

The prediction (6.8) is thus successful if

$$C = 0.54 \left(\frac{R_\lambda}{15} \right)^{\frac{1}{2}} = 1.33,$$

which is quite close to the value 1.5 suggested by Kolmogoroff from a comparison with measurements made by Dryden. Other predictions from the theory of local isotropy (Batchelor 1947) have already been verified by the experiments described in I.

7. MEASUREMENT OF THE TRIPLE CORRELATION

It was shown in II that the two alternative deductions from the hypothesis of limited self-preservation lead to different predictions about the triple velocity correlation function k . According to the first solution, the decay law is such that R_λ is constant, and

$$f'' + f' \left(\frac{4}{\psi} + \frac{5\psi}{2} \right) + 5f + \frac{1}{2}R_\lambda \left(k' + \frac{4}{\psi}k \right) = 0 \quad (7.1)$$

for $r < l$. Solving (7.1) for k ,

$$R_\lambda k(\psi) = -2(f' + \psi f) - \frac{3}{\psi^4} \int_0^\infty \psi^5 f' d\psi, \quad (7.2)$$

so that if f is measured, k can be calculated. On the other hand, the second solution leads to a decay law which makes R_λ tend to a constant value, and to the equations

$$f'' + \frac{4}{\psi} f' + (\frac{1}{2} + 0.23R_\lambda) \psi f' + 5f = 0, \quad (7.3)$$

$$k = \frac{0.46}{\psi^4} \int_0^\infty \psi^5 f' d\psi, \quad (7.4)$$

which can be solved to give both f and k in terms of R_λ . Both solutions give the correct value of k_0''' .

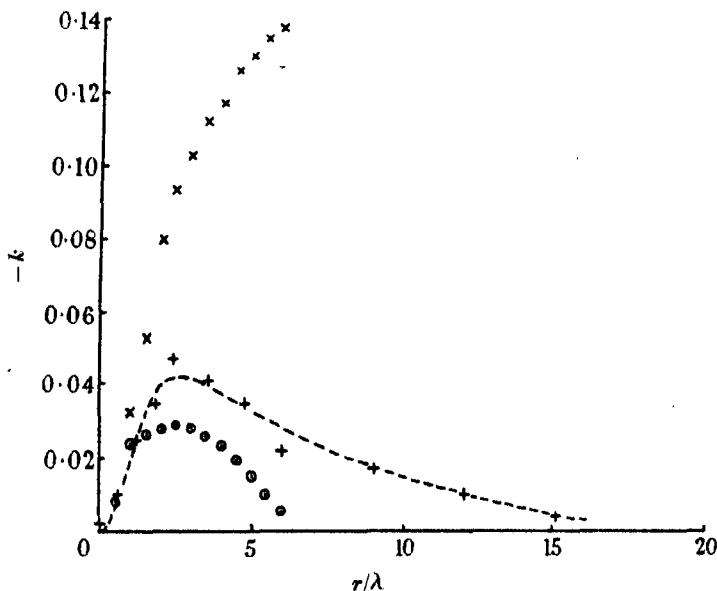


FIGURE 12. Triple correlation. + Experimental. $\odot$ 1st solution; $\times$ 2nd solution, both deduced from limited self-preservation.

A measurement of k for various values of r therefore provides a means of choosing between the two alternative deductions from the hypothesis of limited self-preservation. Figure 12 shows measurements of k at $x/M = 40$, for $M = 2.54$ cm., $U = 643$ cm.sec. $^{-1}$, and while no great accuracy is claimed for the measurements, they make it clear that the first solution is correct. The function k calculated from (7.2) and (6.1) by numerical integration of the values of g measured under the same conditions is shown in figure 12 and has the same shape as the measured curve for $r/\lambda < 4$. The ordinates of the calculated and measured curves differ in magnitude but this is probably due to the sensitivity of the integral in (7.2) to an error in the value of λ . Calculations of k from (7.3) and (7.4) with the appropriate value of R_λ are shown in figure 12 and do not give a curve of the correct shape. Hence, from the evidence of this and preceding section, it may be concluded that the initial period of decay is characterized by a decay law such that R_λ is constant and by the relation (7.1) between the double and triple correlations.

The measurements of k shown in figure 12 have considerable intrinsic interest, although the authors hope to be able to make more accurate determinations. When r is small, k is necessarily proportional to r^3 , and the curvature evidently decreases to zero rapidly as r increases. The maximum value of k is near $r/\lambda = 2.5$, and is followed by a slow fall to zero as r become large. The measurements of k are everywhere negative, which is the basis for an assumption that $\int_0^\infty k dr < 0$ used in II in the deduction that a completely self-preserving solution must occur when the time of decay is large.

8. INTERPRETATION OF THE INITIAL PERIOD

This paper would not be complete without some consideration of the physical processes occurring in the initial period of decay, although such considerations can be little more than speculation at the present time. The fundamental difficulty is to explain or deduce the law of energy decay found for this period. No acceptable deduction of this decay law—except that based on the assumption of limited self-preservation, which merely transfers the difficulty—has yet been put forward. Dimensional arguments have been used to deduce the energy decay law (Taylor 1935; Dryden 1943), but these assume that there is a single length characteristic of the turbulence and the experiments herein show this to be untrue. Such arguments can be successful if, and only if, they can show that the total amount of work done against Reynolds stresses created by the smaller scale velocity fluctuations is proportional to u^3/λ . Since the dissipation of energy by viscosity is proportional to $\nu u'^2/\lambda^2$, consistency of the two expressions leads to $R_\lambda = \text{constant}$.

But once the decay law of the initial period is accepted, it is possible to understand—in the mathematical sense, at all events—why the period cannot continue indefinitely. For instance it was shown (see (6.3)) that

$$\int_0^\infty \psi^4 f(\psi) d\psi \propto t^{-1}$$

in the initial period. Near the origin, $f(\psi) \approx 1 - \frac{1}{2}\psi^2$ so that if f is to remain single-valued and positive, the above integral cannot decrease beyond a certain limit. Physically, the termination of the initial period seems to be a consequence of a continual narrowing of the range of sizes of eddies comprising the energy spectrum. At one end of the scale there is the length λ , which increases as $\sqrt{t}$. λ^{-2} is the mean square wave-number of sinusoidal velocity fluctuations, weighted according to their contribution to the total energy, so that λ is representative of the eddies of large wave-number, i.e. of the small eddies. At the other end of the scale is the integral scale L , representative of the largest eddies. L increases less rapidly than λ , so that the range is continually diminishing. A crisis develops, and whatever its nature, the net result is to reduce the rate of increase of λ .

The larger eddies lose their energy chiefly through the action of the inertia terms in the Navier-Stokes equations by transfer to smaller eddies, whereas the smaller

eddies are dissipated chiefly by the action of viscosity. At the end of a long period of decay, when the disparity in size between the largest and smallest eddies has been reduced appreciably and the Reynolds number of the larger eddies has diminished, viscosity becomes a significant factor in the reduction in energy of all the eddies. It is reasonable to expect a fundamental change in the decay law then to occur. During the transitional period the inertia terms continue to play some part in the transfer of energy away from the larger eddies, but the Reynolds number is decreasing with time, and in the final period of decay viscosity dominates the mechanics of the turbulence. The large negative value at the minimum of the correlation function g which holds in the final period (see equation (6.7) and figure 5) is an indication that the eddies existing in the final period are more uniform in type and size than in the initial period.

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Interaction of mesons with a potential field

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The Takata-Saketani wave equation for mesons is developed to allow the solution of a variety of problems concerning the behaviour of charged vector mesons in an electrostatic field. In particular the form of the radial wave equations is discussed. The general elastic scattering problem is also formulated, and the Born approximation for the phases is discussed for the Coulomb field, for which, as is known, no exact solution is possible. The exact treatment of scattering by a spherical well is considered. This is the only case for which exact treatment in terms of known functions seems practicable, and might be of service in indicating the limits of the validity of approximate processes in other cases.

1. INTRODUCTION

A variety of formalisms are in current use for the treatment of the electromagnetic interaction of mesons. The original wave equation of Proca (1936) as developed by various authors, with its emphasis on the field aspect, is perhaps not the most suitable for the single particle problems, which are the subject of this paper. The first matrix treatment, due to Kemmer (1939) is more suitable in this respect, and leads to a general formalism quite analogous to the Dirac electron theory. For particular problems it suffers from the defect that of the ten wave function components four are redundant (cf. Booth & Wilson (1940)). The most suitable formalism for problems in which the specific meson interaction is not concerned appears to be that developed almost simultaneously by Sakata & Taketani (1940*a, b*) and Tamm (1940), which shows that, with the elimination of the redundant components from the Kemmer theory, the wave equation can still be expressed in Hamiltonian form. A clear exposition of the general theory has been given by Heitler (1943).

The plan of this paper is, then, the systematic development of the Sakata-Taketani theory, as applied to the various basic one particle meson problems, and in particular to the quest for bound states in a given potential field, and to the formulation of the scattering problems. Throughout the development will be very analogous to that for the Dirac electron.

2. FUNDAMENTAL EQUATIONS

We start from the Sakata-Taketani Hamiltonian form, of which a full discussion is given by Heitler (1943)

$$H = e\phi + mc^2\beta + \beta(1 + \eta)\mathbf{p}^2/2m - \beta\eta(\boldsymbol{\sigma} \cdot \mathbf{p})^2/m. \quad (1)$$

Here the σ 's are the spin matrices for particles of spin 1, connected by the relations

$$\sigma_i\sigma_j - \sigma_j\sigma_i = i\epsilon_{ijk}\sigma_k = i\sigma_{ij} \quad \text{and} \quad \sigma_i^2 = \sigma_i, \quad (2)$$

where we use the usual double suffix summation convention and ϵ -symbol. β , η and a third matrix ϵ (Heitler's notation) are related like the usual Pauli 2×2 spin matrices, and are connected with the meson charge. e and m are the meson charge and rest mass and ϕ is the field potential. The generalization to a general electro-magnetic field is found on replacing, as usual, $\mathbf{p}$ by $\mathbf{p} - \frac{e}{c} \mathbf{A}$, and adding the term

$$\frac{e\hbar}{2mc} \beta(1 + \eta) (\boldsymbol{\sigma} \cdot \mathbf{H}),$$

where $\mathbf{A}$, $\mathbf{H}$ represent the field vector potential, and magnetic intensity respectively. The wave equation is of the usual form

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi, \quad (3)$$

where ψ is a vector in the 6- (= 2×3) dimensional space of the β , σ representations. An essential difference from the Dirac theory is now that H is not Hermitian. This is linked with the fact that the charge density is given by $\rho = \psi^\dagger \beta \psi$, so that the average value of an observable Q is given by $\int \psi^\dagger \beta Q \psi d\tau$. The condition for an operator Q to represent an observable is in fact that βQ be Hermitian, and this condition is satisfied by H .

3. MOTION IN A CENTRAL FIELD

We begin directly with the case of motion in a central field. This can as in the Dirac particle case be developed in two ways. We may either, as with Darwin (1928), use the explicit spherical harmonic forms for the angular wave functions, and hence derive the radial wave equations, or we may work entirely algebraically with the appropriate operators as in Dirac's original treatment. We shall in fact compromise to some extent between the two methods.

In the first instance it may easily be verified that for a spherically symmetric field, $\phi = \phi(r)$, $\mathbf{M} = \mathbf{m} + \mathbf{s} = \hbar(\mathbf{k} + \boldsymbol{\sigma})$ is in fact a constant of the motion. Here we denote $\mathbf{m} = \mathbf{r} \times \mathbf{p} = \hbar\mathbf{k}$ for the orbital angular momentum, and $\mathbf{s} = \hbar\boldsymbol{\sigma}$ for the spin angular momentum of the particle. The stationary states, if any, can thus be partially classified by the values of the energy E , total angular momentum $\mathbf{M}$, and angular momentum component in a given direction, M_z . For the last two we introduce the quantum numbers j and m .

From general principles we then know that a state of given j and m may be found by superposing states with orbital quantum number $l = (j - 1), j, (j + 1)$, i.e. states which are separately eigenstates of both $\mathbf{m}^2$ and $\mathbf{M}^2$, though the complete wave function is not in general an eigenstate of $\mathbf{m}^2$, which is not a constant of the motion. For the algebraic treatment it is convenient to consider the operator $(\mathbf{k} \cdot \boldsymbol{\sigma})$. It may easily be verified using the relation

$$\sigma_i \sigma_j \sigma_k + \sigma_k \sigma_j \sigma_i = \sigma_i \delta_{jk} + \sigma_k \delta_{ij} \quad (4)$$

deducible from (2) that

$$(\mathbf{k} \cdot \boldsymbol{\sigma})^3 = ((\mathbf{k} \cdot \boldsymbol{\sigma}) + 1) \mathbf{k}^2 - 2(\mathbf{k} \cdot \boldsymbol{\sigma})^2 - (\mathbf{k} \cdot \boldsymbol{\sigma}) \quad (5)$$

or if we introduce $K = ((\boldsymbol{\sigma} \cdot \mathbf{k}) + 1)$ then $K^3 = l(l+1)K + K^2$. From this it follows that the eigenvalues of $(\boldsymbol{\sigma} \cdot \mathbf{m})$ are $\hbar l$, $-\hbar$ and $-(l+1)\hbar$, corresponding to the states $j = l+1$, l , and $(l-1)$ respectively. We shall denote the angular wave functions in spin space by the symbol u with appropriate suffices, so that for given j and m we have the three independent wave functions

$$u_{j-1, j, m}, \quad u_{j+1, j, m} \quad \text{and} \quad u_{j, j, m},$$

which are such that

$$\begin{aligned} (\mathbf{k} \cdot \boldsymbol{\sigma}) u_{j-1, j, m} &= (j-1) u_{j-1, j, m}, & (\mathbf{k} \cdot \boldsymbol{\sigma}) u_{j, j, m} &= -u_{j, j, m}, \\ (\mathbf{k} \cdot \boldsymbol{\sigma}) u_{j+1, j, m} &= -(j+2) u_{j+1, j, m}. \end{aligned} \quad (6)$$

If we take an explicit representation for the σ in which, say, σ_z is diagonal with matrix

$$\sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

and the phase factors are chosen so that

$$\sigma_x = 1/\sqrt{2} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}, \quad \sigma_y = 1/\sqrt{2} \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & i \\ i & -i & 0 \end{pmatrix}, \quad (7)$$

then the expressions for the normalized angular eigenfunctions are easily deduced:

$$\left. \begin{aligned} u_{j-1, j, m} &= \begin{pmatrix} \sqrt{\left\{ \frac{(j+m)(j+m-1)}{2j(2j-1)} \right\}} Y_{j-1, m-1} \\ \sqrt{\left\{ \frac{(j-m-1)(j-m)}{2j(2j-1)} \right\}} Y_{j-1, m+1} \\ -\sqrt{\left\{ \frac{(j-m)(j+m)}{j(2j-1)} \right\}} Y_{j-1, m} \end{pmatrix}, \\ u_{j+1, j, m} &= \begin{pmatrix} \sqrt{\left\{ \frac{(j+1-m)(j+2-m)}{2(j+1)(2j+3)} \right\}} Y_{j+1, m-1} \\ \sqrt{\left\{ \frac{(j+1+m)(j+2+m)}{2(j+1)(2j+3)} \right\}} Y_{j+1, m+1} \\ \sqrt{\left\{ \frac{(j+1-m)(j+1+m)}{(j+1)(2j+3)} \right\}} Y_{j+1, m} \end{pmatrix}, \\ u_{j, j, m} &= \begin{pmatrix} \sqrt{\left\{ \frac{(j+m)(j-m+1)}{2j(j+1)} \right\}} Y_{j, m-1} \\ -\sqrt{\left\{ \frac{(j-m)(j+m+1)}{2j(j+1)} \right\}} Y_{j, m+1} \\ \frac{m}{\sqrt{j(j+1)}} Y_{j, m} \end{pmatrix}. \end{aligned} \right\} \quad (8)$$

Here $Y_{l,m}$ is used to denote the normalized spherical harmonic, defined by

$$Y_{l,m}(\theta, \phi) = \frac{1}{\sqrt{(2\pi)}} \mathcal{P}_{l,m} e^{im\phi},$$

where $\mathcal{P}_{l,m} = \sqrt{\left\{ \frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \right\}} \frac{(1-x^2)^{im}}{2^l l!} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l, \quad (x = \cos \theta),$

is the normalized associated Legendre function (m positive or negative).

4. OPERATORS $(\boldsymbol{\sigma} \cdot \mathbf{p})^2$, $(\boldsymbol{\sigma} \cdot \mathbf{x})^2$, ETC.

In the wave equation (3) the operator $(\boldsymbol{\sigma} \cdot \mathbf{p})^2$ occurs, and is indeed the chief novelty of the meson theory. It is the term called by Heitler (1943) the gyroscopic term, describing the motion of a gyroscope with inertia tensor $t_{ik} = \sigma_i \sigma_k + \sigma_k \sigma_i$. The direct evaluation of this operator applied to the angular wave-functions is a matter of some elaboration, and an algebraic approach is preferable. The operators $(\boldsymbol{\sigma} \cdot \mathbf{x})^2$ and $(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})$, which also occur in the theory may be considered at the same time. Corresponding to the eigenvalue 1 of the spin, there are no simple properties associated with the squares of the spin operators—it is always necessary to go to the third order to obtain useful commutation properties. In particular the relation (4) is often helpful. The details of the derivation of the results below will not be given as this is quite straightforward.

(a) Operator $(\boldsymbol{\sigma} \cdot \mathbf{x})^2$

Using the usual commutation relationships and (4) it may be established that

$$(\boldsymbol{\sigma} \cdot \mathbf{m})(\boldsymbol{\sigma} \cdot \mathbf{x})^2 + (\boldsymbol{\sigma} \cdot \mathbf{x})^2(\boldsymbol{\sigma} \cdot \mathbf{m}) = (\boldsymbol{\sigma} \cdot \mathbf{m})\mathbf{x}^2 - 3\hbar(\boldsymbol{\sigma} \cdot \mathbf{x})^2 + 2\hbar\mathbf{x}^2.$$

If we define

$$C = (\boldsymbol{\sigma} \cdot \mathbf{x})^2(\boldsymbol{\sigma} \cdot \mathbf{m}) - (\boldsymbol{\sigma} \cdot \mathbf{m})(\boldsymbol{\sigma} \cdot \mathbf{x})^2,$$

then

$$(\boldsymbol{\sigma} \cdot \mathbf{m})C + C(\boldsymbol{\sigma} \cdot \mathbf{m}) = -3\hbar C. \quad (9)$$

Applying this result in the various cases we find (dropping the suffix m)

$$Cu_{j,j} = 0, \quad Cu_{j-1,j} = \lambda u_{j+1,j}, \quad Cu_{j+1,j} = \mu u_{j-1,j}. \quad (10)$$

From the first it follows that $(\boldsymbol{\sigma} \cdot \mathbf{x})^2 u_{j,j} = \mathbf{x}^2 u_{j,j} = r^2 u_{j,j}$. For the other two states C has exchanging properties. The values of λ, μ will of course depend on the phase constants of the representation. They are determined by

$$\lambda = u_{j+1,j}^\dagger C u_{j-1,j}, \quad \mu = u_{j-1,j}^\dagger C u_{j+1,j}$$

and from the properties of C , $\lambda = -\mu^*$. The product $\lambda\mu$ is found from the value of $C^2 = -r^4 \{(\boldsymbol{\sigma} \cdot \mathbf{m} + \frac{3}{2}\hbar)^2 - \frac{1}{2}\hbar^2\}$, so that for operation on $u_{j-1,j}$ or $u_{j+1,j}$

$$C^2 = -j(j+1)\hbar^2 r^4 = \lambda\mu.$$

We choose the values, corresponding with the explicit form for the u 's already given, so that

$$Cu_{j-1,j} = \sqrt{j(j+1)} \hbar r^2 u_{j+1,j}, \quad Cu_{j+1,j} = -\sqrt{j(j+1)} \hbar r^2 u_{j-1,j}. \quad (11)$$

or alternatively

$$\left. \begin{aligned} (\boldsymbol{\sigma} \cdot \mathbf{x})^2 u_{j-1,j} &= \frac{r^2}{2j+1} [(j+1) u_{j-1,j} + \sqrt{j(j+1)} u_{j+1,j}], \\ (\boldsymbol{\sigma} \cdot \mathbf{x})^2 u_{j+1,j} &= \frac{r^2}{2j+1} [j u_{j+1,j} + \sqrt{j(j+1)} u_{j-1,j}]. \end{aligned} \right\} \quad (12)$$

(b) Operator $(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})$

For the operator $(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})$ we can establish the relation

$$\begin{aligned} (\boldsymbol{\sigma} \cdot \mathbf{m} + \tfrac{3}{2}\hbar)(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p}) + (\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{m} + \tfrac{3}{2}\hbar) \\ = (\boldsymbol{\sigma} \cdot \mathbf{m} + 2\hbar)(\mathbf{x} \cdot \mathbf{p}) + i\{(\boldsymbol{\sigma} \cdot \mathbf{m} + \hbar)^2 - \hbar^2\}. \end{aligned} \quad (13)$$

An exchanging operator D similar to C above can be formed. It is

$$D = (\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{m}) - (\boldsymbol{\sigma} \cdot \mathbf{m})(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})$$

and satisfies

$$(\boldsymbol{\sigma} \cdot \mathbf{m})D + D(\boldsymbol{\sigma} \cdot \mathbf{m}) = -3\hbar D. \quad (14)$$

For the state $j = l$, $D = 0$, and from (6) we immediately conclude

$$(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p}) u_{j,j} = (\mathbf{x} \cdot \mathbf{p} - i\hbar) u_{j,j} = -i\hbar u_{j,j} \left(r \frac{d}{dr} + 1 \right). \quad (15)$$

For the states $j = l \pm 1$, since $(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})$ commutes with $\mathbf{M}$ the form

$$(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p}) u_{j-1,j} = \alpha u_{j-1,j} + \beta u_{j+1,j}, \quad (\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p}) u_{j+1,j} = \gamma u_{j-1,j} + \delta u_{j+1,j} \quad (16)$$

must hold (the property of D excludes a term in $u_{j,j}$). The coefficients $\alpha, \beta, \gamma, \delta$ can be determined using (12), and (13), when the result of multiplying both sides of (16) by $(\boldsymbol{\sigma} \cdot \mathbf{x})^2$ is used. Here it must be noted that $(\boldsymbol{\sigma} \cdot \mathbf{x})^3 = r^2(\boldsymbol{\sigma} \cdot \mathbf{x})$. It is finally found that

$$\left. \begin{aligned} (\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p}) u_{j-1,j} &= \frac{-i\hbar(j+1)}{2j+1} \left\{ r \frac{d}{dr} - (j-1) \right\} \left[u_{j-1,j} + \sqrt{\frac{j}{j+1}} u_{j+1,j} \right], \\ (\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p}) u_{j+1,j} &= \frac{-i\hbar j}{2j+1} \left\{ r \frac{d}{dr} + (j+2) \right\} \left[u_{j+1,j} + \sqrt{\frac{j+1}{j}} u_{j-1,j} \right]. \end{aligned} \right\} \quad (17)$$

(c) Operator $(\boldsymbol{\sigma} \cdot \mathbf{p})^2$

An exactly similar technique can be used in this case. The relation comparable to (13)

$$(\boldsymbol{\sigma} \cdot \mathbf{m})(\boldsymbol{\sigma} \cdot \mathbf{p})^2 + (\boldsymbol{\sigma} \cdot \mathbf{p})^2(\boldsymbol{\sigma} \cdot \mathbf{m}) = (\boldsymbol{\sigma} \cdot \mathbf{m})\mathbf{p}^2 - 3\hbar(\boldsymbol{\sigma} \cdot \mathbf{p})^2 + 2\hbar\mathbf{p}^2 \quad (18)$$

now holds, and the operator $B = (\boldsymbol{\sigma} \cdot \mathbf{p})^2(\boldsymbol{\sigma} \cdot \mathbf{m}) - (\boldsymbol{\sigma} \cdot \mathbf{m})(\boldsymbol{\sigma} \cdot \mathbf{p})^2$ has similar properties to the C defined earlier, such that

$$(\boldsymbol{\sigma} \cdot \mathbf{m})B + B(\boldsymbol{\sigma} \cdot \mathbf{m}) = -3\hbar B. \quad (19)$$

$B = 0$ for the state $j = l$, for which

$$(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = \mathbf{p}^2. \quad (20)$$

B has again the property of interchanging the states $j = l \pm 1$ (it is this property which corresponds with the spin orbit coupling caused by the appearance of $(\boldsymbol{\sigma} \cdot \mathbf{p})^2$ in the Hamiltonian). This shows that, for example

$$Bu_{j-1,j} = u_{j+1,j} L,$$

where L is a second-order differential operator in (d/dr) . The explicit form of L is perhaps easiest found by considering the relation

$$(\boldsymbol{\sigma} \cdot \mathbf{m})(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = i[(\mathbf{x} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p})^2 - (\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})\mathbf{p}^2] \quad (21)$$

together with the result for $(\boldsymbol{\sigma} \cdot \mathbf{x})(\boldsymbol{\sigma} \cdot \mathbf{p})$ already established. This leads to

$$Bu_{j-1,j} = -\hbar^2 \sqrt{j(j+1)} u_{j+1,j} E_{j-1}^2, \quad Bu_{j+1,j} = \hbar^2 \sqrt{j(j+1)} u_{j-1,j} G_{j+1}^2, \quad (22)$$

or alternatively

$$\left. \begin{aligned} (\boldsymbol{\sigma} \cdot \mathbf{p})^2 u_{j-1,j} &= \frac{j+1}{2j+1} \mathbf{p}^2 u_{j-1,j} - \frac{\sqrt{j(j+1)}}{(2j+1)} \hbar^2 u_{j+1,j} E_{j-1}^2, \\ (\boldsymbol{\sigma} \cdot \mathbf{p})^2 u_{j+1,j} &= \frac{j}{(2j+1)} \mathbf{p}^2 u_{j+1,j} - \frac{\sqrt{j(j+1)}}{(2j+1)} \hbar^2 u_{j-1,j} G_{j+1}^2. \end{aligned} \right\} \quad (23)$$

The differential operators E_{j-1}^2 , G_{j+1}^2 are defined by

$$E_{j-1}^2 = d^2 - \frac{2j-1}{r} d + \frac{(j-1)(j+1)}{r^2} = \left(d - \frac{j}{r}\right) \left(d - \frac{j-1}{r}\right), \quad (24)$$

$$G_{j+1}^2 = d^2 + \frac{2j+3}{r} d + \frac{j(j+2)}{r^2} = \left(d + \frac{j+1}{r}\right) \left(d + \frac{j+2}{r}\right), \quad (25)$$

where $d = d/dr$.

If we also define

$$D_j^2 = d^2 + \frac{2}{r} d - \frac{j(j+1)}{r^2} = \left(d + \frac{j+2}{r}\right) \left(d - \frac{j}{r}\right) = \left(d - \frac{j-1}{r}\right) \left(d + \frac{j+1}{r}\right),$$

$$\left. \begin{aligned} \text{then} \quad E_{j-1}^2 D_{j-1}^2 &= D_{j+1}^2 E_{j-1}^2, \quad G_{j+1}^2 E_{j-1}^2 = D_{j-1}^2 E_{j-3}^2 G_{j-1}^2 \\ \text{and} \quad G_{j+1}^2 D_{j+1}^2 &= D_{j-1}^2 G_{j+1}^2. \end{aligned} \right\} \quad (26)$$

These results will be found useful later in deriving the radial equations.

5. RADIAL WAVE EQUATIONS

We have now carried out all the formal work necessary to reduce the wave equation to radial form, and shall proceed to find the radial equations directly, rather than by trying to cast the Hamiltonian into radial form. The wave function may be regarded as made up of two components in the charge-space $\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$, where ψ_1 , ψ_2 are both still vectors in the three-dimensional spin space, assuming we are dealing with a vector meson field. The particular (ψ_1, ψ_2) for a given ψ will,

of course, depend on the representation chosen for the charge operators. Generally we take

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \eta = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (27)$$

As contribution to ψ for a given j and m we shall have

$$\psi_1 = f_{j-1,j,m}(r) u_{j-1,j,m} + f_{j+1,j,m}(r) u_{j+1,j,m} + f_{j,j,m}(r) u_{j,j,m} \quad (28)$$

and a similar expression for ψ_2 with, say, g in place of f . As we have already seen in the investigation of the operators, these components subdivide into two non-combining sets—that for $u_{j,j}$ and that from $u_{j-1,j}$ and $u_{j+1,j}$. The suffix m may be dropped as it does not enter the equations. The equation for $f_{j,j}$ provides no difficulty being simply the Klein-Gordon equation. For the other states it might be thought that, apart from the higher order, the position was no worse than for the Dirac electron. In this latter case, with the present notation, a solution is found in which

$$\psi_1 = f_{j-\frac{1}{2},j} u_{j-\frac{1}{2},j}, \quad \psi_2 = g_{j+\frac{1}{2},j} u_{j+\frac{1}{2},j},$$

thus involving two simultaneous first order equations in $f_{j-\frac{1}{2},j}$, $g_{j+\frac{1}{2},j}$. No such separation is possible in the meson case. The basic reason for this is the difference in parity in the electron case between $u_{j-\frac{1}{2},j}$ and $u_{j+\frac{1}{2},j}$; no such difference exists between $u_{j-1,j}$ and $u_{j+1,j}$. Lacking such a separation we must then expect four simultaneous second-order equations for the combining functions $f_{j-1,j}$, $f_{j+1,j}$, $g_{j-1,j}$, $g_{j+1,j}$. The total eighth order is only apparent, and as remarked by Tamm (1940), using different representations, two simultaneous equations of the second order can be found to describe these radial functions.

The radial equations for the stationary states may be found explicitly quite simply by substituting the form (28) for ψ in $H\psi = E\psi$, and using the expression for $(\sigma \cdot \mathbf{p})^2$ (23). There results

$$\left. \begin{aligned} \text{(i)} \quad & \left(E - V - E_0 + \frac{\hbar^2}{2m} D_{j-1}^2 \right) f_{j-1,j} = \frac{\hbar^2}{2m(2j+1)} [D_{j-1}^2 g_{j-1,j} + 2\sqrt{j(j+1)} G_{j+1}^2 g_{j+1,j}], \\ \text{(ii)} \quad & \left(E - V - E_0 + \frac{\hbar^2}{2m} D_{j+1}^2 \right) f_{j+1,j} = \frac{\hbar^2}{2m(2j+1)} [-D_{j+1}^2 g_{j+1,j} + 2\sqrt{j(j+1)} E_{j-1}^2 g_{j-1,j}], \\ \text{(iii)} \quad & \left(E - V + E_0 - \frac{\hbar^2}{2m} D_{j-1}^2 \right) g_{j-1,j} = -\frac{\hbar^2}{2m(2j+1)} [D_{j-1}^2 f_{j-1,j} + 2\sqrt{j(j+1)} G_{j+1}^2 f_{j+1,j}], \\ \text{(iv)} \quad & \left(E - V + E_0 - \frac{\hbar^2}{2m} D_{j+1}^2 \right) g_{j+1,j} = -\frac{\hbar^2}{2m(2j+1)} [-D_{j+1}^2 f_{j+1,j} + 2\sqrt{j(j+1)} E_{j-1}^2 f_{j-1,j}], \end{aligned} \right\} \quad (29)$$

where $E_0 = mc^2$, and $V = e\phi$. Before discussing in detail the solution for particular cases we give briefly the general method of reduction. Introducing

$$\left. \begin{aligned} f_1 &= f_{j-1,j} + g_{j-1,j}, & g_1 &= f_{j+1,j} + g_{j+1,j}, \\ f_2 &= f_{j-1,j} - g_{j-1,j}, & g_2 &= f_{j+1,j} - g_{j-1,j}, \end{aligned} \right\} \quad (30)$$

and transferring to 'meson units'—the analogue of Hartree atomic units with the appropriate rest mass, we find the simplified equations,

$$\left. \begin{aligned} \text{(i)} \quad (2j+1) \left[(E-V)f_1 + \left(\frac{j+1}{2j+1} D_{j-1}^2 - E_0 \right) f_2 \right] &= -\sqrt{j(j+1)} G_{j+1}^2 g_2, \\ \text{(ii)} \quad (2j+1) \left[(E-V)f_2 + \left(\frac{j}{2j+1} D_{j-1}^2 - E_0 \right) f_1 \right] &= \sqrt{j(j+1)} G_{j+1}^2 g_1, \\ \text{(iii)} \quad (2j+1) \left[(E-V)g_1 + \left(\frac{j}{2j+1} D_{j+1}^2 - E_0 \right) g_2 \right] &= -\sqrt{j(j+1)} E_{j-1}^2 f_2, \\ \text{(iv)} \quad (2j+1) \left[(E-V)g_2 + \left(\frac{j+1}{2j+1} D_{j+1}^2 - E_0 \right) g_1 \right] &= \sqrt{j(j+1)} E_{j-1}^2 f_1. \end{aligned} \right\} \quad (31)$$

Two of the functions, say, f_2 , g_2 can now be directly eliminated. The elimination is tedious, but direct, leading to two second-order equations. Perhaps a simpler method of simplification is that which leads to equations of the form found by Tamm (1940). To find these we define

$$F_1 = \frac{r}{\sqrt{j(j+1)}} \{ \sqrt{j(j+1)} g_1 - \sqrt{j} f_1 \}, \quad G_1 = r \{ \sqrt{j} g_1 + \sqrt{j(j+1)} f_1 \} \quad (32)$$

and similarly F_2 , G_2 .

Then, writing $v = (E-V)/\sqrt{j(j+1)}$, $E'_0 = E_0/j(j+1)$, the equations (31) may be transformed to yield

$$\left. \begin{aligned} vF_1 - E'_0 F_2 &= \frac{1}{r} \left(G'_2 + \frac{1}{r} F_2 \right), \\ vG_1 - E_0 G_2 &= -G'_2 - \frac{1}{r} \left(\frac{d}{dr} - \frac{1}{r} \right) F_2, \\ vG_2 - E'_0 G_1 &= \frac{1}{r^2} G_1 + \frac{1}{r} \left(\frac{d}{dr} + \frac{1}{r} \right) F_1, \\ vF_2 - E_0 F_1 &= - \left(\frac{d^2}{dr^2} - \frac{2}{r^2} \right) F_1 - \frac{1}{r} \left(\frac{d}{dr} - \frac{2}{r} \right) G_1. \end{aligned} \right\} \quad (33)$$

Two simultaneous equations of the second order may be found, for example, by eliminating F_2 and G_1 . We find

$$\left. \begin{aligned} \{ \Lambda - 2E'_0 r^2 / (1 + E'_0 r^2) \} F_1 + R G_2 &= 0, \quad \Lambda G_2 + R F_1 = 0, \\ \text{where} \quad R &= r \frac{d}{dr} \{ v / (1 + E'_0 r^2) \}, \\ \Lambda &= E'_0 \left(r \frac{d}{dr} + 1 \right) \left\{ r \frac{d}{dr} / (1 + E'_0 r^2) \right\} + v^2 r^2 / (1 + E'_0 r^2) - E_0. \end{aligned} \right\} \quad (34)$$

It is not proposed to discuss these equations further here. No exact solutions to them have been found, other than in the field-free case, and, as noted in a recent paper by Bartlett (1947), their numerical treatment would present a huge problem.

It may be noted that the form of the equations is similar to those treated by Stueckelberg (1932) by Jeffreys' approximation. This technique might prove valuable under suitable conditions when the Born approximation is not applicable. In the case of a Coulomb field it may quite directly be shown that in the neighbourhood of the origin the equations have an essential singularity. This point was noted by Corben & Schwinger (1940) from a wave treatment and by Tamm (1940) using equations similar to ours. The latter makes it clear that the singularity arises from the meson magnetic moment, producing a term of order $1/r^3$ in the second order radial equation which is the approximate form of (34) in the neighbourhood of the origin.

6. FORMULATION OF SCATTERING PROBLEM FOR MESONS

We now consider the formulation of the single particle elastic scattering problem for mesons. The problem is analogous to that treated by Mott (1929, 1932), for Dirac electrons, and similar polarization effects may be expected.

The incident particles are supposed to have momentum p along the z -axis. They may be represented, using the same β - and σ -representations as previously by the wave function

$$\psi_1 = \begin{pmatrix} A \\ B \\ C \end{pmatrix} e^{ipz/\hbar}. \quad (35)$$

As in the electron case the other charge-space component ψ_2 need not be explicitly introduced, and the scattering phenomenon can be described in terms of ψ_1 alone. In fact, as is seen from (1)

$$\psi_2 = \frac{E - E_0}{E + E_0} \begin{pmatrix} A \\ B \\ -C \end{pmatrix} e^{ipz/\hbar}, \quad (36)$$

where E is the energy of the incident particle so that $E^2 = E_0^2 + c^2 p^2$. Thus the charge density in the incident beam, is given by

$$\rho = e\psi^\dagger \beta \psi = e(\psi_1^* \psi_1 - \psi_2^* \psi_2) = e \frac{4EE_0}{(E + E_0)^2} \{|A|^2 + |B|^2 + |C|^2\}, \quad (37)$$

and the current density in the z -direction may be verified from the general expression to be

$$j_z = \rho v_z = \rho \frac{c^2 p}{E} = \frac{4E_0^2}{(E + E_0)^2} \frac{p}{m} \{|A|^2 + |B|^2 + |C|^2\} e. \quad (38)$$

In the scattered wave, which can be regarded as made up of spherical waves it will equally be necessary, for the asymptotic behaviour, to consider only the wave function ψ_1 .

The incident plane wave may be expanded in a set of spherical waves. For this purpose it is convenient to consider separately the different incident polarizations.

From (8) it is found, using the orthogonal properties of the coefficients of the u 's that

$$\left. \begin{aligned} \sqrt{\left\{\frac{l+2}{2(2l+1)}\right\}} u_{l,l+1,1} + \sqrt{\left\{\frac{(l-1)}{2(2l+1)}\right\}} u_{l,l-1,1} + \sqrt{\frac{1}{2}} u_{l,l,1} &= \begin{pmatrix} Y_{l,0} \\ 0 \\ 0 \end{pmatrix}, \\ \sqrt{\left\{\frac{l+2}{2(2l+1)}\right\}} u_{l,l+1,-1} + \sqrt{\left\{\frac{(l-1)}{2(2l+1)}\right\}} u_{l,l-1,-1} - \sqrt{\frac{1}{2}} u_{l,l,-1} &= \begin{pmatrix} 0 \\ Y_{l,0} \\ 0 \end{pmatrix}, \\ -\sqrt{\left\{\frac{l+1}{2(2l+1)}\right\}} u_{l,l+1,0} + \sqrt{\left\{\frac{l}{2(2l+1)}\right\}} u_{l,l-1,0} &= \begin{pmatrix} 0 \\ 0 \\ Y_{l,0} \end{pmatrix}. \end{aligned} \right\} \quad (39)$$

For $l = 0$, $l = 1$ the general formulae have to be replaced by special ones. The terms $u_{l,l-1,\pm 1}$ do not in fact appear for $l = 0, 1$, and $u_{l,l,\pm 1}$, $u_{l,l-1,0}$ for $l = 0$.

It is convenient to consider the various polarizations of the incident wave in turn.

(a) *Spin along positive z-axis* ($m = 1$). If ψ_1 denotes the complete stationary state wave function for incident and scattered beams, which is supposed expanded in the usual form

$$\psi_1 = \sum_j (u_{j-1,j,1} f_{j-1,j,1} + u_{j+1,j,1} f_{j+1,j,1} + u_{j,j,1} f_{j,j,1}) \quad (40)$$

and the incident wave I_1 is given by

$$I_1 = e^{ikz} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad k = p/\hbar, \quad (41)$$

then

$$\begin{aligned} (\psi_1 - I_1) = \sum_l \{ & u_{l,l+1,1} [f_{l,l+1,1} - i^l \sqrt{\{2\pi(l+2)\}} j_l(kr)] \\ & + u_{l,l-1,-1} [f_{l,l-1,-1} - i^l \sqrt{\{2\pi(l-1)\}} j_l] + u_{l,l,1} [f_{l,l,1} - i^l \sqrt{\{2\pi(2l+1)\}} j_l] \}, \end{aligned} \quad (42)$$

where again the middle term does not occur for $l = 0, 1$ nor the last for $l = 0$. The j_l denote the usual spherical Bessel functions. Now in general each of the f 's will involve two arbitrary constants—one of these will be determined by the regularity condition at $r = 0$. The other is determined by the fact that asymptotically the right-hand side of (42) must represent only a scattered wave. If the asymptotic form of say $f_{l,l+1,1}$ is given by

$$f_{l,l+1,1} \sim \frac{C_{l,l+1,1}}{kr} \sin(kr - \frac{1}{2}l\pi + \delta_{l,l+1,1}), \quad (43)$$

(this form will be valid provided the scattering potential falls off quickly enough at large distances), and similar expressions hold for the other f 's, then from the asymptotic condition

$$\left. \begin{aligned} C_{l,l+1,1} &= i^l \sqrt{\{2\pi(l+2)\}} \exp(i\delta_{l,l+1,1}), \\ C_{l,l-1,1} &= i^l \sqrt{\{2\pi(l-1)\}} \exp(i\delta_{l,l-1,1}), \\ C_{l,l,1} &= i^l \sqrt{\{2\pi(2l+1)\}} \exp(i\delta_{l,l,1}). \end{aligned} \right\} \quad (44)$$

The asymptotic form for the scattered wave can then be found. It may be written in the form

$$\left. \begin{aligned} \psi_{11} &= SF_1(\theta), \\ \psi_{12} &= SF_2(\theta) e^{2i\phi} \quad \text{with} \quad S = e^{ikr}/r, \\ \psi_{13} &= SF_3(\theta) e^{i\phi}, \end{aligned} \right\} \quad (45)$$

where, in terms of the usual Legendre functions

$$\left. \begin{aligned} F_1(\theta) &= \frac{1}{2ik} \Sigma \left[\frac{1}{2}(l+2)(e^{2i\delta_{l,l+1,1}} - 1) + \frac{1}{2}(l-1)(e^{2i\delta_{l,l-1,1}} - 1) + \frac{1}{2}(2l+1)(e^{2i\delta_{l,l,1}} - 1) \right] P_l(\cos \theta), \\ F_2(\theta) &= \frac{1}{2ik} \Sigma \left[\frac{1}{2(l+1)}(e^{2i\delta_{l,l+1,1}} - 1) + \frac{1}{2l}(e^{2i\delta_{l,l-1,1}} - 1) - \frac{2l+1}{2l(l+1)}(e^{2i\delta_{l,l,1}} - 1) \right] P_l^2(\cos \theta), \\ F_3(\theta) &= \frac{\sqrt{2}}{2ik} \Sigma \left[-\frac{(l+2)}{2(l+1)}(e^{2i\delta_{l,l+1,1}} - 1) + \frac{(l-1)}{2l}(e^{2i\delta_{l,l-1,1}} - 1) + \frac{2l+1}{2l(l+1)}(e^{2i\delta_{l,l,1}} - 1) \right] P_l^1(\cos \theta). \end{aligned} \right\} \quad (46)$$

The properties of the scattered beam are thus determined in terms of the phases of the various angular momentum components into which it may be resolved.

The cases where $m = -1$, and $m = 0$ for the incident beam may be similarly treated. The results are quoted below.

(b) *Incident particle spin in negative z-direction* ($m = -1$). With the same notation as previously

$$\left. \begin{aligned} C_{l,l+1,-1} &= i^l \sqrt{\{2\pi(l+2)\}} \exp(i\delta_{l,l+1,-1}), \\ C_{l,l-1,-1} &= i^l \sqrt{\{2\pi(l-1)\}} \exp(i\delta_{l,l-1,-1}), \\ C_{l,l,-1} &= -i^l \sqrt{\{2\pi(2l+1)\}} \exp(i\delta_{l,l,-1}), \end{aligned} \right\} \quad (47)$$

and for the scattered wave

$$\psi_{11} = SF_2(\theta) e^{-2i\phi}, \quad \psi_{12} = SF_1(\theta), \quad \psi_{13} = -SF_3(\theta) e^{-i\phi}. \quad (48)$$

$$(c) \quad m = 0. \quad \left. \begin{aligned} C_{l,l+1,0} &= -i^l \sqrt{\{4\pi(l+1)\}} \exp(i\delta_{l,l+1,0}), \\ C_{l,l-1,0} &= i^l \sqrt{\{4\pi l\}} \exp(i\delta_{l,l-1,0}), \end{aligned} \right\} \quad (49)$$

and for the scattered wave

$$\psi_{11} = SH_1(\theta) e^{-i\phi}, \quad \psi_{12} = -SH_1(\theta) e^{i\phi}, \quad \psi_{13} = SH_3(\theta), \quad (50)$$

$$\left. \begin{aligned} \text{where} \quad H_1(\theta) &= \frac{1}{2\sqrt{2}ik} \Sigma (e^{2i\delta_{l,l+1,0}} - e^{2i\delta_{l,l-1,0}}) P_l^1(\cos \theta), \\ H_3(\theta) &= \frac{1}{2ik} \Sigma [(l+1)(e^{2i\delta_{l,l+1,0}} - 1) + l(e^{2i\delta_{l,l-1,0}} - 1)] P_l(\cos \theta). \end{aligned} \right\} \quad (51)$$

It should be noted that the independence on m of the radial equations, together with the similarity of the asymptotic form of the radial wave functions for $m = \pm 1$, ensures that the phases for $m = \pm 1$ are identical. Different values, however, appear for $m = 0$. The use of F_1, F_2, F_3 for $m = -1$, with no distinction from the case $m = 1$, is thus justified.

The general case when the incident wave is given by

$$\psi_1 = \begin{pmatrix} A \\ B \\ C \end{pmatrix} e^{ikz},$$

may now be obtained by superposition. If the scattered wave is given by

$$\psi_1 = \frac{e^{ikr}}{r} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix},$$

then

$$\left. \begin{aligned} u_1 &= AF_1(\theta) + BF_2(\theta)e^{-2i\phi} + CH_1(\theta)e^{-i\phi}, \\ u_2 &= AF_2(\theta)e^{2i\phi} + BF_1(\theta) - CH_1(\theta)e^{i\phi}, \\ u_3 &= AF_3(\theta)e^{i\phi} - BF_3(\theta)e^{-i\phi} + CH_3(\theta). \end{aligned} \right\} \quad (52)$$

The differential scattering cross-section is given by $\Sigma |u|^2$. This will depend on the polarization of the incident meson beam as determined by the ratios of A , B and C . It is clear that the polarization effects, described by Mott for the electron, will also arise for the meson. Thus, for example, if the incident beam is completely unpolarized, which we may represent by putting $|A| = |B| = |C| = 1/\sqrt{3}$, it will not follow that $|u_1| = |u_2| = |u_3|$, and the scattered beam will generally exhibit some preferential direction of spin.

In order to consider the matter in greater detail it is necessary to investigate how the direction of the spin axis of the meson is determined by A , B and C . For this purpose the polar angles of the spin direction will be denoted by (χ, ω) . The spin measured along this direction has the value 1, so that

$$(\sigma_x \sin \chi \cos \omega + \sigma_y \sin \chi \sin \omega + \sigma_z \cos \chi) \begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} A \\ B \\ C \end{pmatrix}. \quad (53)$$

Using the representation (7) for the σ 's we find the normalized set of constants

$$A = \cos^2 \frac{\chi}{2} e^{-i\omega}, \quad B = \sin^2 \frac{\chi}{2} e^{i\omega}, \quad C = \frac{1}{\sqrt{2}} \sin \chi. \quad (54)$$

With the use of these values the differential cross-section in the direction (θ, ϕ) when the incident beam is polarized in the direction (χ, ω) is found to be

$$\begin{aligned} \Sigma |u|^2 &= (\cos^4 \frac{1}{2}\chi + \sin^4 \frac{1}{2}\chi) \{ |F_1|^2 + |F_2|^2 + |F_3|^2 \} + \frac{1}{2} \sin^2 \chi \{ 2 |H_1|^2 + |H_3|^2 \} \\ &\quad + \frac{1}{2} \sin^2 \chi \cos 2(\omega - \phi) \{ F_1^* F_2 + F_2^* F_1 - |F_3|^2 \} \\ &\quad + \frac{1}{\sqrt{2}} \sin \chi \{ i \sin(\omega - \phi) + \cos \chi \cos(\omega - \phi) \} \{ (F_1^* + F_2^*) H_1 + F_3^* H_3 \} \\ &\quad + \text{conj. complex}. \end{aligned} \quad (55)$$

The case of an unpolarized incident beam is obtained by averaging over χ and ω , and has the obvious value

$$\Sigma |u|^2 = \frac{2}{3} \{ |F_1|^2 + |F_2|^2 + |F_3|^2 \} + \frac{1}{3} \{ 2 |H_1|^2 + |H_3|^2 \}. \quad (56)$$

7. BORN APPROXIMATION FOR SCATTERING OF VECTOR MESONS

The Born approximation formula for the scattering of vector mesons by a potential field has been considered by several authors. The first approximation formula was derived originally by Laporte (1938) and later by Massey & Corben (1939), using wave theory in both cases. The second approximation was found by Ma (1942) using the Kemmer matrix technique. These approximate methods yield a finite solution for the scattering cross-section by a Coulomb field, whereas as we have seen, no exact solution to this problem exists. In an attempt to assess the validity of the approximation we investigate its deduction by considering the decomposition into harmonic components.

From equations (29), using meson units, the Born approximation for the phases may be easily deduced. It is convenient to alter the form of the equations. Thus

$$2\sqrt{j(j+1)}\{E_{j-1}^2 \times (i) - D_{j+1}^2 \times (ii) - (2j+1)D_{j+1}^2 \times (iv)\}$$

yields

$$2\sqrt{j(j+1)}\{E_{j-1}^2\{(E-E_0-V)f_{j-1,j}\} - D_{j+1}^2\{(E-E_0-V)f_{j+1,j}\} - (2j+1)D_{j+1}^2\{(E+E_0-V)g_{j+1,j}\} = 0,$$

and from similar other relations

$$\left. \begin{aligned} D_{j-1}^2\{(E-E_0-V)f_{j-1,j}\} + 2\sqrt{j(j+1)}\{G_{j+1}^2\{(E-E_0-V)f_{j+1,j}\} - (2j+1)D_{j-1}^2\{(E+E_0-V)g_{j-1,j}\} &= 0, \\ 2\sqrt{j(j+1)}\{E_{j-1}^2\{(E+E_0-V)g_{j-1,j}\} - D_{j+1}^2\{(E+E_0-V)g_{j+1,j}\} - (2j+1)D_{j+1}^2\{(E-E_0-V)f_{j+1,j}\} &= 0, \\ D_{j-1}^2\{(E+E_0-V)g_{j-1,j}\} + 2\sqrt{j(j+1)}\{G_{j+1}^2\{(E+E_0-V)g_{j+1,j}\} - (2j+1)D_{j-1}^2\{(E-E_0-V)f_{j-1,j}\} &= 0. \end{aligned} \right\} \quad (57)$$

Combining these with (29), and writing $k^2 = \frac{E^2 - E_0^2}{E_0}$ (E, E_0 in meson units) we find

$$\left. \begin{aligned} (D_{j-1}^2 + k^2)f_{j-1,j} &= \frac{1}{2E_0(2j+1)} [D_{j-1}^2(Vg_{j-1,j}) + 2\sqrt{j(j+1)}\{G_{j+1}^2(Vg_{j+1,j}) - (2j+1)D_{j-1}^2(Vf_{j-1,j}) + 2(E+E_0)(2j+1)Vf_{j-1,j}\}, \\ (D_{j+1}^2 + k^2)f_{j+1,j} &= \frac{1}{2E_0(2j+1)} [2\sqrt{j(j+1)}\{E_{j-1}^2(Vg_{j-1,j}) - D_{j+1}^2(Vg_{j+1,j}) - (2j+1)D_{j+1}^2(Vf_{j+1,j}) + 2(2j+1)(E+E_0)Vf_{j+1,j}\}, \\ (D_{j-1}^2 + k^2)g_{j-1,j} &= \frac{1}{2E_0(2j+1)} [-D_{j-1}^2(Vf_{j-1,j}) - 2\sqrt{j(j+1)}\{G_{j+1}^2(Vf_{j+1,j}) + (2j+1)D_{j-1}^2(Vg_{j-1,j}) + 2(2j+1)(E-E_0)Vg_{j-1,j}\}, \\ (D_{j+1}^2 + k^2)g_{j+1,j} &= \frac{1}{2E_0(2j+1)} [-2\sqrt{j(j+1)}\{E_{j-1}^2(Vf_{j-1,j}) + D_{j+1}^2(Vf_{j+1,j}) + (2j+1)D_{j+1}^2(Vg_{j+1,j}) + 2(2j+1)(E-E_0)Vg_{j+1,j}\}. \end{aligned} \right\} \quad (58)$$

If V can be treated as small, a first approximation to the solution will be found by giving to f and g on the right-hand side their undisturbed values, i.e. their values in the harmonic decomposition of the incident plane wave in the scattering problem. The approximation thus found should agree with the Born approximation found by other methods.

With this assumption the equations are all of the form

$$(D_l^2 + k^2)f(r) = -F(r)$$

the general solution to which is

$$f = c_1 j_l(kr) + c_2 n_l(kr) + k \left[j_l(kr) \int_0^r n_l(ks) s^2 F(s) ds - n_l(kr) \int_0^r j_l(ks) s^2 F(s) ds \right], \quad (59)$$

where j_l, n_l are the spherical Bessel functions. If the unperturbed solution is $f = j_l(kr)$, and the perturbed solution is such that $f \sim \frac{1}{kr} \sin(kr - \frac{1}{2}l\pi + \delta_l)$, then if the integrals are both small, we may write

$$\delta_l = k \int_0^\infty j_l(ks) s^2 F(s) ds. \quad (60)$$

For the vector meson it will appear that this latter condition is always unsatisfied, through the divergence of $\int_0^r n_l(ks) s^2 F(s) ds$. This divergence may not be a very important one as it is solely due to the singularity of the Coulomb field at the origin, and will be removed if the field be supposed cut-off at some distance, say of the order of the meson classical radius $\sim 10^{-15}$ cm. There can be little physical meaning in effects produced by singularities within this radius, and it can be regarded as a purely formal difference between electrons and vector mesons that the relativistic magnetic moment of the latter makes it necessary explicitly to introduce the cut-off.

Whilst, apart from the general theoretical difficulties, the qualitative introduction of a cut-off seems quite permissible, the matter can scarcely be left to rest there. It must be investigated how the phases and cross-sections will depend on the cut-off radius. Such a variation is bound to occur at sufficiently high energies and in this way it might even be hoped that experimental results on the Coulomb elastic scattering of vector mesons could eventually throw light on the quantitative behaviour of the cut-off. This possibility has, however, been considered too distant to justify detailed calculations at the present stage. In general it may be noted that the idea of the cut-off fits well into the statistical theories (e.g. Rosen (1947)) now being considered by various authors, and if it could be made quantitative, might provide information for their development.

8. BORN APPROXIMATION. COULOMB FIELD

The Born approximation for the phases will now be briefly discussed for the particular case of the Coulomb field. For a repulsive field of charge Z , we have $V = Ze^2/r$. It is as usual convenient to consider the various polarizations of the incident beam in turn.

(a) $m = +1$. Apart from an insignificant proportionality factor the zero approximation functions in this case are given by

$$\left. \begin{aligned} f_{j-1,j,1}^{(0)} &= j_{j-1}(kr), \\ f_{j+1,j,1}^{(0)} &= -\sqrt{\{j/(j+1)\}} j_{j+1}(kr), \\ f_{j,j,1}^{(0)} &= i\sqrt{\{(2j+1)/(j+1)\}} j_j(kr). \end{aligned} \right\} \quad (61)$$

It is convenient to work with ordinary units, using, however, as units of length the particle wave length $1/k$. To determine $\delta_{j-1,j,1}$ we then have the equation

$$(D_{j-1}^2 + 1)f_{j-1,j,1} = \frac{Ze^2k}{2E_0(2j+1)} \left[D_{j-1}^2 \left(\frac{s^2}{r} f_{j-1,j,1}^{(0)} \right) + 2\sqrt{\{j(j+1)\}} G_{j+1}^2 \left(\frac{s^2}{r} f_{j+1,j,1}^{(0)} \right) \right. \\ \left. - (2j+1) D_{j-1}^2 \left(\frac{1}{r} f_{j-1,j,1}^{(0)} \right) + \frac{2E_0}{(E-E_0)} \frac{(2j+1)}{r} f_{j-1,j,1}^{(0)} \right], \quad (62)$$

where $s^2 = \frac{E-E_0}{E+E_0}$.

Introducing the notation

$$\alpha = \frac{Ze^2}{\hbar c}, \quad k_0 = \frac{mc}{\hbar}, \quad \beta = \frac{v}{c} = \sqrt{1 - \frac{E_0^2}{E^2}}, \quad (63)$$

then, after some reduction, (62) can be put in the form

$$(D_{j-1}^2 + 1)f_{j-1,j,1} = \frac{2\alpha j_{j-1}(r)}{\beta} + \frac{\alpha k}{k_0} \frac{1}{(2j+1)} \\ \times \left[\frac{(2j+1)(1-s^2)}{r^2} \left\{ \frac{(j-1)j_{j-1}}{r} - j_j \right\} - \frac{s^2 j}{r^3} \{3j_{j+1} - 2(j-1)j_{j-1}\} \right]. \quad (64)$$

The first term on the right-hand side gives the usual Rutherford scattering. The second term gives to the first order in α the effects of meson magnetic moment, etc. The method used in deducing (64) has removed the usual second order relativity term $-\frac{\alpha^2}{r^2} j_{j-1}$, which would have to be replaced if Z is not small.

Ignoring the Rutherford term, the relativity correction to the phase is given by

$$\delta_{j-1,j,1} = \frac{\alpha k}{k_0} \int_0^\infty \left[\frac{s^2 j}{2j+1} \frac{j_{j-1}\{3j_{j+1} - 2(j-1)j_{j-1}\}}{r} - (1-s^2) j_{j-1} \left\{ \frac{(j-1)j_{j-1}}{r} - j_j \right\} \right] dr. \quad (65)$$

Some care must be observed in carrying out the integration for the case $j = 1$, when the integrals multiplying $(j-1)$ are in fact divergent. As is shown later this corresponds with the singularity of $\nabla^2 V$ at the origin in a Coulomb field. The final result is that

$$\delta_{j-1,j,1} = -\frac{s^2 \alpha k}{2k_0} \frac{1}{(j+1)} \quad (j = 1, 2, \dots). \quad (66)$$

With $\alpha = 1/137$ we see that all these phases will be less than 1, until $k \neq 100k_0$. This implies a wave-length of the order of 10^{-15} cm. for the incident mesons, or an energy of the order of 10^4 MeV. At such an energy the assumed departure from the Coulomb law at very small distances $\sim 10^{-15}$ cm. must have begun to take effect. In fact, if the cut-off is made a distance a , then the lower limit is the integral for δ becomes ka which is $O(1)$ for the case considered. The cut-off ultimately leads to a diminution in the phases as the incident energy is further increased. The asymptotic form is

$$\delta_{j-1,j+1} \sim \frac{\alpha}{4ak_0} \frac{j}{ka}.$$

In general then we see that, provided α is small, the perturbation method in itself will not lead to serious errors in computing the relativistic effects, unless the cut-off distance is materially less than 10^{-15} cm. Deviation from its predicted results up to an energy of the order of 10^3 MeV would be an indication of departure from the Coulomb field.

The derivation of the remaining phases will not be discussed in detail. The results are merely quoted below

$$\left. \begin{aligned} \delta_{j+1,j+1} &= \frac{s^2 \alpha k}{2k_0} \frac{1}{j} & (j = 1, 2, \dots), \\ \delta_{j-1,j,0} &= -\frac{s^2 \alpha k}{2k_0} \frac{1}{j} & (j = 1, 2, \dots), \\ \delta_{j+1,j,0} &= \frac{s^2 \alpha k}{2k_0} \frac{1}{(j+1)} & (j = 1, 2, \dots), \\ &= 0 & (j = 0). \end{aligned} \right\} \quad (67)$$

(b) Phases for $m = -1$ are equal to those for $m = 1$. For the $j = l$ components the relativistic phase changes are of order α^2 , being similar to those for scalar mesons. In certain cases (scattering by heavy nuclei) such terms are important, but they will be ignored in the present investigation.

The conditions under which these phases are likely to be valid have already been discussed. When they are small, we may replace $e^{i\delta}$ by $(1 + i\delta)$, and hence determine the total angular distribution of the scattering from (46) and (51). Considering only the relativistic terms,

$$\left. \begin{aligned} F_1 &= -\frac{s^2 \alpha k}{2k_0} \cos^2 \frac{1}{2} \theta, \\ F_2 &= \frac{s^2 \alpha k}{2k_0} \cos^2 \frac{1}{2} \theta, \\ F_3 &= \frac{s^2 \alpha k}{2k_0} \frac{1}{\sqrt{2}} (\cot \frac{1}{2} \theta - \sin \theta) \quad H_1 = -F_3, \quad H_2 = 2F_1. \end{aligned} \right\} \quad (68)$$

It may be of interest to note that in the derivation of these functions only the $l = 0, 1$ waves contribute to F_1 and H_2 . For higher l -values there is complete cancellation between the $l = (j+1)$ and $l = (j-1)$ component, in our approximation.

The total differential cross-section may be found by adding the Rutherford term $-\frac{\alpha}{2k\beta} \operatorname{cosec}^2 \frac{1}{2}\theta$ to F_1 and H_3 , and using (56). The result agrees with that found by various authors, Laporte (1938), Massey & Corben (1939)

$$Q = \left(\frac{Ze^2}{2mv^2} \right)^2 \frac{E_0^2}{E^2} \operatorname{cosec}^4 \frac{1}{2}\theta + \frac{2}{3} \left(\frac{Ze^2}{2mc^2} \right)^2 \cot^2 \frac{1}{2}\theta. \quad (69)$$

It can of course be most speedily derived with absorption and emission matrix elements and the spur technique (Sakata & Taketani (1940a)).

9. SECOND-ORDER WAVE EQUATION—PERTURBATION TREATMENT

The sources of the various phases may be to some extent clarified by a consideration of the second-order wave equation, which in any case provides a speedier derivation of the angular distribution of the scattered waves. For a charged vector meson in a potential field it is found from the first order equation

$$[E - V - mc^2\beta - \beta(1 + \eta)\mathbf{p}^2/2m + \beta\eta(\boldsymbol{\sigma} \cdot \mathbf{p})^2/m]\psi = 0, \quad (70)$$

by operating on it with

$$E - V + mc^2\beta + \beta(1 + \eta)\mathbf{p}^2/2m - \beta\eta(\boldsymbol{\sigma} \cdot \mathbf{p})^2/m.$$

The equation is found in the form

$$(\nabla^2 + k^2)\psi = \left[\frac{2EV}{\hbar^2 c^2} - \frac{V^2}{\hbar^2 c^2} - \frac{1}{2mc^2}\beta(1 + \eta)(\nabla^2 V - V\nabla^2) + \frac{\beta\eta}{mc^2}\{(\boldsymbol{\sigma} \cdot \nabla)^2 V - V(\boldsymbol{\sigma} \cdot \nabla)^2\} \right] \psi. \quad (71)$$

A solution to this equation representing an incident wave

$$\psi_1^{(0)} = \begin{pmatrix} A \\ B \\ C \end{pmatrix} e^{ikz} \quad \text{and} \quad \psi_2^{(0)} = s^2 \begin{pmatrix} A \\ B \\ -C \end{pmatrix} e^{ikz},$$

together with a scattered wave, treated as a perturbation, may be formed by replacing ψ on the right-hand side by $\psi^{(0)}$ (see, for example, Mott & Massey (1933)). The equation for ψ_1 then has the form

$$(\nabla^2 + 1)\psi_1 = U(r, \theta, \phi)e^{iz}, \quad (72)$$

where once more the unit of length $1/k$ is used.

This gives as the scattered wave

$$\psi_1 = u(\theta, \phi)e^{ir}/r, \quad (73)$$

$$\text{where} \quad u(\theta, \phi) = -\frac{1}{4\pi} \int e^{i\mathbf{K}\mathbf{r}' \cos \gamma} U(\mathbf{r}') d\mathbf{r}', \quad K = 2 \sin \frac{1}{2}\theta, \quad (74)$$

γ being the angle between the directions (θ', ϕ') and $(\frac{1}{2}(\pi - \theta), \pi + \phi)$. U is easily found in the general case. For the Coulomb field, when $V = Ze^2/r$, care must be taken to

add the term $\nabla^2 V = -4\pi Ze^2 \delta(r)$ and a similar term in the expression for $(\sigma \cdot \nabla)^2 V$. These δ -function terms correspond to the peculiarity mentioned earlier in the evaluation of the phases $\delta_{0,1,\pm 1}$ and $\delta_{0,1,0}$. It may easily be verified, with this precaution, that the expressions for F_1 , H_1 , etc. are as found before.

10. SCATTERING BY SPHERICAL WELL

Special theoretical interest attaches to the case of scattering by a spherical potential well, as this is the only form of field for which an exact solution can readily be given. We consider a well of the form

$$V = -V_0 \quad (r < r_0), \quad V = 0 \quad (r > r_0), \quad (75)$$

and write
$$k^2 = \frac{E^2 - E_0^2}{\hbar^2 c^2}, \quad k'^2 = \frac{(E + V_0)^2 - E_0^2}{\hbar^2 c^2}.$$

The equations for the radial wave functions outside the well are then of the form

$$(D_{j-1}^2 + k^2) \begin{Bmatrix} f_{j-1,j} \\ g_{j-1,j} \end{Bmatrix} = 0, \quad (D_{j+1}^2 + k^2) \begin{Bmatrix} f_{j+1,j} \\ g_{j+1,j} \end{Bmatrix} = 0, \quad (D_j^2 + k^2) \begin{Bmatrix} f_{j,j} \\ g_{j,j} \end{Bmatrix} = 0. \quad (76)$$

Inside the well similar equations hold with k replaced by k' . Each of the functions contains two arbitrary constants: externally one is determined by the asymptotic behaviour at infinity, and internally one from the behaviour at the origin. The remaining two constants are fixed by the continuity conditions across the boundary $r = r_0$.

As in the earlier problems we approach the case of general meson spin by superposing the simple ones, and consider firstly $m = 1$, so that the incident wave is determined by

$$\psi_1 = e^{ikz} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}. \quad (77)$$

From the asymptotic conditions it may then easily be verified that outside the well ψ_1 is of the form

$$\begin{aligned} \psi_1 = \sqrt{\frac{\pi}{2}} \sum_j i^j [& -i \sqrt{j+1} \{ e^{2i\delta_{j-1,j,1}} h_{j-1}^{(1)}(kr) + h_{j-1}^{(2)}(kr) \} u_{j-1,j,1} \\ & + i \sqrt{j} \{ e^{2i\delta_{j+1,j,1}} h_{j+1}^{(1)}(kr) + h_{j+1}^{(2)}(kr) \} u_{j+1,j,1} \\ & + \sqrt{2j+1} \{ e^{2i\delta_{j,j,1}} h_j^{(1)}(kr) + h_j^{(2)}(kr) \} u_{j,j,1}]. \end{aligned} \quad (78)$$

Here $h_n^{(1)}$, $h_n^{(2)}$ are used to denote the spherical Hankel functions of the first and second kinds, defined so that

$$h_n^{(1),(2)}(\rho) = \sqrt{\left(\frac{\pi}{2\rho}\right)} H_{n+\frac{1}{2}}^{(1),(2)}(\rho). \quad (79)$$

From the condition at $r = 0$, inside the well ψ_1 must be of the form

$$\psi_1 = \sum_j \{ a_{j-1,j,1} j_{j-1}(k'r) u_{j-1,j,1} + a_{j+1,j,1} j_{j+1}(k'r) u_{j+1,j,1} + a_{j,j,1} j_j(k'r) u_{j,j,1} \}. \quad (80)$$

The forms for ψ_2 may immediately be deduced from the above, but as they are rather cumbersome will not be quoted here.

Boundary conditions

To complete the solution the α 's and β 's must be determined by the boundary conditions at $r = r_0$. It is not immediately evident, as for Schrödinger and Dirac particles, what these boundary conditions must be. However they may be derived, either from the degenerate form of the field equations, or by considering the normal component of the current density vector, the conservation of which must be contained in the field equations. There is, in general, no need for charge density to be continuous across a boundary, a condition in fact satisfied for Schrödinger and Dirac particles but not by mesons. In this respect the hydrodynamical analogue to the meson behaviour at a potential barrier is the formation of shock waves in compressible fluid flow.

The simplest physical approach is to consider the normal component of the current density vector. The space components of this vector are given (cf. Heitler (1943)) by

$$i_k = \psi^\dagger \frac{1+\eta}{2mc} p_k \psi - \psi^\dagger \frac{\eta}{2mc} \{ \sigma_k(\mathbf{p} \cdot \boldsymbol{\sigma}) + (\mathbf{p} \cdot \boldsymbol{\sigma}) \sigma_k \} \psi + \frac{i}{2mc} \psi^\dagger (\mathbf{p} \times \boldsymbol{\sigma})_k \psi + \text{conj. complex.} \quad (81)$$

It may immediately be verified that for a steady state they satisfy the continuity equation

$$\text{div } \mathbf{i} = 0.$$

It is convenient to modify this expression so as to render obvious the requirements for the continuity of i_n . This may most compactly be performed by introducing the operators

$$\left. \begin{aligned} \alpha_k &= p_k + \sigma_k(\mathbf{p} \cdot \boldsymbol{\sigma}) - (\mathbf{p} \cdot \boldsymbol{\sigma}) \sigma_k = p_k + i(\mathbf{p} \times \boldsymbol{\sigma})_k, \\ \beta_k &= p_k - \sigma_k(\mathbf{p} \cdot \boldsymbol{\sigma}) - (\mathbf{p} \cdot \boldsymbol{\sigma}) \sigma_k. \end{aligned} \right\} \quad (82)$$

If $\tau_k = (1 - 2\sigma_k^2)$, so that $\tau_k^2 = 1$, then with the help of the σ -commutation properties (4) it follows that

$$\tau_k \beta_k = \alpha_k, \quad \tau_k \alpha_k = \beta_k.$$

From (81) we have $2mc i_k = (\psi_1 + \tau_k \psi_2)^\dagger (\alpha_k \psi_1 + \beta_k \psi_2) + \text{conj.}$ (83)

So, in general, the normal current density component i_n will be continuous across a boundary if $(\psi_1 + \tau_n \psi_2)$ and $(\alpha_n \psi_1 + \beta_n \psi_2)$ are both continuous.

The investigation of the boundary conditions does not strictly end here, for the conservation of momentum requires separate proof. This may be obtained from a straightforward demonstration that (83) is equivalent to the degenerate form of the field equations, which will be omitted here.

The boundary conditions may be simplified slightly in the present case where the potential is a constant. With the help of the field equations it will here be found that

$$\beta_k \psi_2 = -s^2 \alpha_k \psi_1, \quad \text{where} \quad s^2 = (E - E_0)/(E + E_0). \quad (84)$$

Thus the second boundary condition may be expressed

$$(1-s) \alpha_n \psi_1 \quad \text{continuous.} \quad (85)$$

Determination of phases

With ψ_1 as given by (78) and (80) the phases $\delta_{j-1,j,1}$, $\delta_{j+1,j,1}$, $\delta_{j,j,1}$ can now be determined from the boundary conditions. The formulae concerned are straightforward but their derivation is long, and only the final results will be quoted. It is useful to define

$$\begin{aligned} A_{j-1,j} &= k'j_j(k'r_0)h_{j-1}^{(1)}(kr_0) - kj_{j-1}(k'r_0)h_j^{(1)}(kr_0), \\ A_{j+1,j} &= k'j_j(k'r_0)h_{j+1}^{(1)}(kr_0) - kj_{j+1}(k'r_0)h_j^{(1)}(kr_0), \end{aligned} \quad (86)$$

$$C_j = \left\{ \frac{k'}{k(1-s^2)} - \frac{k}{k'(1-s'^2)} \right\} \frac{j_j(k'r_0)h_j^{(1)}(kr_0)}{r_0} = \frac{V_0}{2E_0ss'} \frac{j_j(k'r_0)h_j^{(1)}(kr_0)}{r_0}, \quad (87)$$

so that $A_{j-1,j} + A_{j+1,j} = (2j+1)(1-ss')C_j$ and $A_{j-1,j} = -A_{j-1,j-2}$. (88)

In terms of these quantities it is found that

$$e^{2i\delta_{j-1,j,1}} = F_1/H, \quad e^{2i\delta_{j+1,j,1}} = G_1/H,$$

where
$$\begin{aligned} F_1 &= A_{j+1,j}A_{j-1,j}^* - 2jss'\{A_{j-1,j}C_j^* - C_jA_{j-1,j}^* - 2(j+1)C_jC_j^*\}, \\ G_1 &= A_{j-1,j}A_{j+1,j}^* - 2(j+1)ss'\{A_{j+1,j}C_j^* - C_jA_{j+1,j}^* - 2jC_jC_j^*\}, \\ H &= -A_{j-1,j}A_{j+1,j} - 4j(j+1)ss'C_jC_j^*. \end{aligned} \quad (89)$$

For the non-relativistic case when $s, s' \rightarrow 0$, it is immediately evident that these formulae reduce to the usual ones for Schrödinger particles with spin 1.

The formula for $\delta_{j,j,1}$ is much simpler, being in fact identical with that for a scalar meson—this peculiarity of the $j = l$ components has already been noted. In this way

$$e^{2i\delta_{j,j,1}} = -\frac{A_{j,j+1}^*}{A_{j,j+1}} = -\frac{A_{j,j-1}^*}{A_{j,j-1}}. \quad (90)$$

The phases for $m = -1$ are identical with those for $m = 1$. This is formally evident from the fact that the asymptotic form for ψ_1 in this case is identical with that for $m = 1$, except for a change in sign of the $j = l$ component. The differential equations governing the radial functions are independent of m , so the phases in the two cases must agree. For $m = 0$ the asymptotic form for ψ_1 is different, and this difference in boundary condition has the effect of altering the phases. Outside the well

$$\psi_1 = \sqrt{\pi} \Sigma i^{j+1} [\sqrt{j} \{e^{2i\delta_{j-1,j,0}} h_{j-1}^{(1)} + h_{j-1}^{(2)}\} + \sqrt{(j+1)} \{e^{2i\delta_{j+1,j,0}} h_{j+1}^{(1)} + h_{j+1}^{(2)}\}]. \quad (91)$$

On applying the boundary conditions at $r = r_0$ it is found that

$$e^{2i\delta_{j-1,j,0}} = F_0/H, \quad e^{2i\delta_{j+1,j,0}} = G_0/H,$$

where
$$\begin{aligned} F_0 &= A_{j+1,j}A_{j-1,j}^* - 2(j+1)ss'\{A_{j-1,j}C_j^* - C_jA_{j-1,j}^* - 2jC_jC_j^*\}, \\ G_0 &= A_{j-1,j}A_{j+1,j}^* - 2jss'\{A_{j+1,j}C_j^* - C_jA_{j+1,j}^* - 2(j+1)C_jC_j^*\}, \end{aligned} \quad (92)$$

and H is as defined before (89).

For the present it has not been considered worth while to apply these formulae to the calculation of the phases in any specific case of spherical well scattering. Their

chief interest might be to provide for one field at least, though admittedly a rather specialized one, an exact picture of the difference in behaviour between relativistic electrons and vector mesons. To this extent they may throw light on the scattering of mesons by other types of field, for which at present only the Born approximation treatment is available. The rather unsatisfactory position of the Coulomb field in this respect has already been discussed.

11. CONCLUDING REMARKS

It has been the aim of this paper to formulate the principal one-body problems for the relativistic meson in interaction with the electro-magnetic field, in a uniform manner and analogously to the standard treatments of the relativistic electron problems. In theory the programme can be satisfactorily carried through, but the fourth order equations involved combined with different polarizations to be considered in each case, make the exact solution of any scattering or stationary state problem a considerable numerical task. However, even for Schrödinger particles exact solutions are formidable enough and frequently not required. It may be that, as with them, a combination of the Born and Jeffreys approximation methods in the general formalism would be adequate for the consideration of many problems of elastic meson scattering by an electric field. The matter must remain to some extent academic until the experimental possibility arises of the observation of such scattering, divorced from scattering by the intrinsic meson field.

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